Second Series. *February, 1914* *Vol. III., No. 2*

THE

PHYSICAL REVIEW.

THE ELECTRICAL DISCHARGE FROM LIQUID POINTS, AND A HYDROSTATIC METHOD OF MEASURING THE ELECTRIC INTENSITY AT THEIR SURFACES.[1]

By John Zeleny.

1. The discharge of electricity from pointed conductors has been studied heretofore only from points made of metal. The assumption is generally made that all of the features of the discharge are independent of the kind of metal of which the point is made. In support of this view may be mentioned the results of Precht,[2] who found that, after a steel needle had been plated with a thin coating of copper, the potential at which the discharge ceased from the needle as well as the current obtained with any voltage, remained the same as before. In a study of the discharge from cylindrical points of different diameters, the writer[3] used platinum points for the two smallest diameters while the others were made of brass, and the results from both kinds of points could be expressed well by the same empirical formula, indicating that the nature of the metal is of no consequence.

2. There are a number of phenomena, however, attending the discharge from pointed conductors which can only be explained by attributing some importance to the surface from which the discharge is taking place. Thus Röntgen[4] found that the potential at which the discharge from a gilded needle began was dependent upon whether a current had been flowing from the point shortly before. Precht[5] gives an example where the beginning potential rose by 25 per cent. at the end of a number of successive determinations.

[1] A preliminary paper on this subject was read before the American Physical Society on December 30, 1910.

[2] J. Precht, Wied. Annalen, 49, p. 150, 1893.

[3] J. Zeleny, Phys. Rev., 25, p. 305, 1907.

[4] W. C. Röntgen, Göttingen Nachrichten, p. 390, 1878.

[5] Loc. cit.

Warburg and Gorton[1] found that the passage of a current from points made of various metals permanently increased the potential at which a discharge begins above that first required when the points were newly made. Subjecting such aged points to various radiations had the effect of temporarily reducing the beginning potentials to their original values. Similar effects were obtained by heating the points in a flame or by heating them to a glow by means of an electric current when they were immersed in oxygen or hydrogen. In some of the cases recorded, the potential increased by over fifty per cent.

Again, it is well known that some impulsive discharges of short duration and at considerable intervals of time may take place from a point at potentials much lower than are required for the first continuous discharge. Precht[2] cites the case of a point cut from a piece of aluminum leaf which gave the first impulsive discharges at + 1,871 and − 1,065 volts, while the continuous currents did not begin until the potentials were raised to + 4,173 and − 2,971 volts.

Such effects as these cannot be ascribed to changes in the circumambient gas, but must be attributed either to some chemical change at the metallic surface, to the accumulation there of some foreign material gathered from the gas, to the formation of or changes in an electric double layer, to changes in the amount of gas absorbed by the point or to changes in the layer of occluded gas. Some of the effects are most likely due to one cause and some to another. In any case, the changes mentioned involve the character of the discharging surface.

3. Although no systematic study has yet been made with points of different metals, it would seem that, for the investigation of influences arising from conditions at the surface of discharge, it would be well not to confine the experiments to metallic points, since metals in general may not differ greatly among themselves as regards some crucial property. In choosing between various materials it was decided to experiment first with liquids because of their radical difference from metals and because of some advantageous properties. A small hemispherical drop protruding from the end of a fine capillary tube may serve as the liquid point. The discharging surface may readily be renewed in this case by simply removing the drop. The chemical nature of the surface may be made quite different by a change of liquid; and this without changing the geometrical shape of the point. The surfaces of such liquid points are necessarily perfectly smooth,[3] but have the disadvantage of being liable to distortion.

[1] E. Warburg and F. R. Gorton, Ann. der Physik, 18, p. 128, 1905.

[2] Loc. cit.

[3] The results of Precht (loc. cit.) and the writer (loc. cit.) indicate that the presence of

APPARATUS USED.

4. The essential parts of the apparatus which was used in the experiments are shown in diagram in Fig. 1. The discharge took place in air

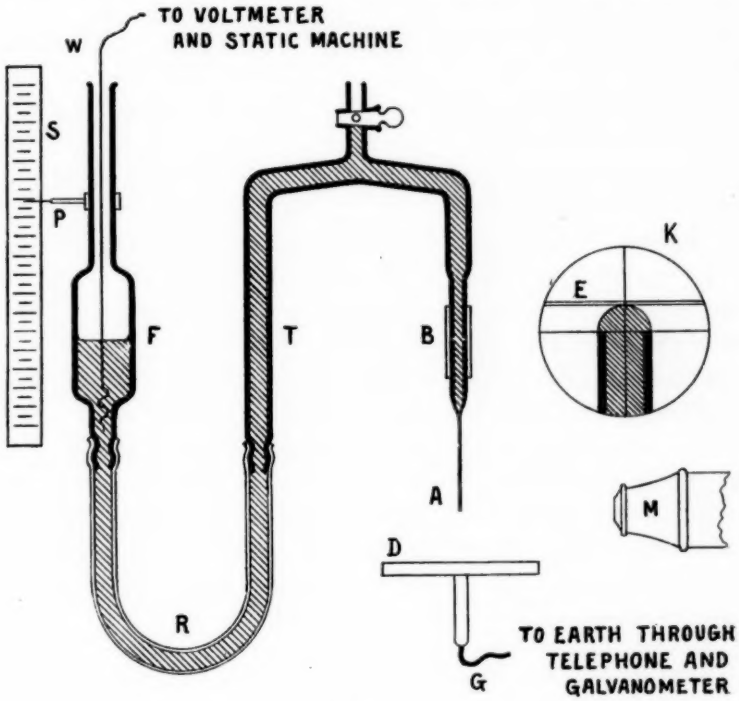

Fig. 1.

Diagram of apparatus.

at atmospheric pressure at the end of the point A, and the current passed to the brass disc D (6.3 cm. in diameter), situated 1.5 cm. below the end of the point, unless otherwise stated. From the disc the current passed first through a telephone receiver, used for detecting intermittence, and then to earth through a shunted D'Arsonval galvanometer whose greatest sensitivity was 3×10^{-9} amperes per scale division. The point A consisted of a cylindrical glass tube whose diameter was nearly constant for a length of 3 cm. and usually did not exceed one millimeter. The free end was broken off squarely across, and the upper end, with the piece of larger tubing from which the fine point had been drawn out, was connected at B by means of a piece of rubber tubing to the glass tube T. This mode of attachment made it easy to exchange points. Finally, the tube T was joined to the glass part F by the rubber tube R.

minor irregularities on the surface is of no consequence and that the general geometrical shape is alone determinative for both the beginning potentials and the current obtained with any potential.

The liquid in the apparatus was connected by the wire W to a high capacity static machine and the voltmeter. The static machine was provided with 15 Leyden jars for steadying the potential, which could be regulated by shunting a part or all of the current to earth through a variable india-ink on paper resistance which was devised for such purposes in this laboratory.[1] A Braun voltmeter reading to 10,000 volts was usually used for measuring the potentials of the points. Its accuracy was tested by comparing its readings with other Braun voltmeters and Kelvin vertical electrostatic voltmeters of various ranges, some of which had been checked for the lower voltages by means of a high potential storage battery. The glass piece F could be raised or lowered by a rack and pinion motion on the stand to which it was clamped. Changes in the vertical position of the liquid surface at F were determined by a cathetometer or from readings of the pointer P on the fixed scale S.

The end of the discharge point was observed with a low power microscope which had an ocular micrometer and was itself carried on a micrometer slide. The latter permitted the measurement of the diameter of a point while in position. With the ocular micrometer a distance was measured from the end of the point equal to the height of meniscus it was proposed to use. The movable cross hairs were left in this position, shown at E in a picture of the field of view drawn at K, and the meniscus was simply raised to the point of tangency to ensure its being of the proper height.

5. The end of a point best suited to the purpose should have a sharp continuous edge, which moreover should lie in a plane which is perpendicular to the axis of the cylinder. Ground ends are not serviceable because the act of grinding breaks off minute chips from the edge and the meniscus on such a point can rarely be raised to a hemispherical form without the liquid crawling over the edge and running up the outside of the tube. The method adopted was to make a fine short scratch on the side of the tube and then break off the tube by a gentle pull. In a rather small fraction of cases the break was sufficiently straight across to permit of use. The roughened portion of the edge, due to the scratch, caused much trouble owing to the overflow of the drop at this point under certain conditions.

The choice of liquid to be used in the apparatus is confined to such liquids as do not leave a residue on evaporation, because the rapid evaporation at the surface of the point soon causes any salt solution to become saturated at this place and to form a deposit. In the experiments to be described in this paper, only one kind of liquid was used, and that

[1] F. Aust, Physik. Zeitschrift, 12, p. 732, 1911.

was a very dilute solution of hydrochloric acid. The conductivity of this was large enough so that no account had to be taken of any fall of potential existing between the voltmeter and the end of the point. Some measurements of the various quantities with which this paper is concerned were made using distilled water and strong hydrochloric acid, and in each case the values obtained were essentially the same as those obtained with the very dilute acid.

Procedure in Experiments.

6. When the liquid surface in F, Fig. 1, is on a level with the end of the tube A, the meniscus at the latter place is flat, it being presupposed that no electric charges are present. As F is raised gradually the meniscus at A bulges out more and more. The vertical height between the meniscus and the surface level in F is a measure of the hydrostatic pressure in the liquid drop. This pressure is a maximum when the radius of curvature of the meniscus is a minimum, which is the case when the meniscus becomes hemispherical.

Knowing r, the radius of the tube A, and h, the height of the liquid necessary to make the meniscus hemispherical, the surface tension T of the liquid can be found from the relation

$$T = \frac{rhdg}{2},$$

where d is the density of the liquid and g the gravity constant. This method of determining T is capable of giving fair results when a well-made point of small diameter is used.

7. If the liquid is gradually charged, the electric force acting at the surface of the meniscus tends to pull the drop outward. This tendency may be counteracted by lowering F until the meniscus is of the same height as it was before being charged. The distance p that the liquid surface was lowered is a measure of the electric pull per unit surface on the meniscus. Expressing this latter in terms of f, the electric intensity at the surface,

$$\frac{f^2}{8\pi} = pdg, \quad \text{or} \quad f = \sqrt{8\pi pdg}.$$

The electric intensity at the surface of the meniscus is thus determined by simply measuring the length of the liquid column whose hydrostatic pressure just counteracts the mechanical pull exerted by the electric field on the surface of the liquid. The electric intensity measured is evidently the largest value obtaining on any part of the liquid surface. If inequalities exist, equilibrium is attained by a distortion of the surface.

The method permits the measurement of the electric intensity in all cases where a definite meniscus can be maintained and has been used for determinations when no current is flowing, when a current is flowing, and under the conditions of the initial current from points.

No difficulty was experienced in getting the pressure reading when the point was charged to a considerable potential, but a great deal of difficulty was experienced with most of the points prepared in obtaining the pressure required to form an uncharged drop whose height approached that necessary to make it a hemisphere. This difficulty arose from the ease with which a drop of such a height overflows up the sides of the tube, the place at which this overflow starts being the scratch on the glass made for breaking off the tube as already mentioned in § 5.

8. The arrangement of a point opposite a plane does not permit of the calculation of the electric intensity at the surface of the point for any voltage. Determinations of the value of this quantity for various potentials below that necessary to start a current were made by the method described with a number of points with hemispherical menisci whose radii ranged from .021 cm. to .054 cm., and where in each case the distance between the end of the charged point and the earthed plane was 1.5 cm.

The results obtained may be stated in the following form: The electric intensity at the end of a point of the form used is sixty per cent. of the intensity that exists at the surface of the inner of two concentric spheres,[1] the smaller of which has a radius equal to the radius of the point in question and is charged to the same potential, while the larger has a radius equal to the distance between the point and plane (1.5 cm.) and is at zero potential.

Measurements of the electric intensity at the point for other distances than 1.5 cm. between the point and plane, made with one point only, gave for the above percentage, 57 per cent. for a distance of 3 cm., and 67.5 per cent. for a distance of 0.5 cm.

These results may be used for finding the electric intensity at the end of metal points of the same shape under the given conditions.

CHARACTERISTICS OF THE DISCHARGE.

9. Some of the phenomena which attend the starting of a current from the points deserve first consideration. Suppose the potential of a liquid point, which has not been used for some minutes, to be increased gradually while the meniscus is kept in a fixed position by proper adjustment of the liquid pressure. When the potential has reached a certain value,

[1] Maxwell, Electricity and Magnetism, Vol. I., 3d ed., p. 189.

whose magnitude depends not only on the diameter of the point but also upon how long the surface of the liquid has stood unused, a momentary discharge takes place, a single click being heard in the telephone receiver and the galvanometer indicating a slight ballistic throw. A faint flash of light appears and the meniscus of the point jerks back into a more flat position, showing that some change has taken place which has resulted in an increase in the surface tension.

This solitary discharge is not repeated at the same voltage (not within some minutes at least) even after the meniscus has been brought to its initial position by added pressure. A second solitary discharge only occurs after the potential has been raised one or more hundred volts. This, too, is accompanied by a fall of the meniscus. Further discharges of the same kind are obtained on increasing the potential by constantly diminishing steps, except that this first stage changes after a few discharges into a second stage where, instead of one discharge following a rise in voltage, several take place at increasing intervals, finally stopping altogether. Going up in potential from this value, a third stage[1] is reached where discharges continue indefinitely, say, at the rate of about one a second. With further increases in voltage the discharges occur closer and closer together until the individual discharges cannot be distinguished either by the galvanometer which shows a steady deflection or by the telephone where a continuous sound is heard, or by the jerks of the meniscus whose upper surface simply appears very blurred through the microscope.

At a still higher potential, a fourth stage is reached with the positive discharge where the meniscus suddenly becomes perfectly motionless, the sound in the telephone ceases, and the galvanometer deflection assumes a smaller steady value. This last stage continues through increases of potential up to the limit used, which was 10,000 volts.

On lowering the potential of the point from its highest value, the steady state (stage four) passes back as suddenly into the intermittent one but this occurs at a somewhat lower voltage than at which it began.

The voltage at which the intermittent current stops is nearly the same as that at which the continuous intermittent stage (stage three above) begins, but is usually a little higher owing to the fact that this stage on the first trial begins at a lower potential than on succeeding trials. However, after a current of some magnitude has been allowed to flow from the point, the voltages at which the intermittent stage stops and then

[1] A slightly different intermediate stage has also been noted where keeping the potential constant, a continuous series of discharges takes place, each consisting of a few discharges in rapid succession, the series being separated by an interval of rest of a second or two.

begins again are usually identical.[1] Potentials obtained under these conditions and the corresponding electric intensities determined at the same time have been taken as the values of these quantities which are necessary to start the discharge. This means that these quantities were measured for the surface conditions existing after the treatment noted.

After the current from a point has been stopped, the initial solitary discharges, mentioned under stage one above, may again come into evidence if the point is left standing for several minutes. The conditions have not been determined under which the first of these solitary discharges would occur at the lowest possible potential. Under the usual procedure of starting an experiment, the liquid surface is agitated during the manipulations and for such a surface the discharge usually begins with the continuous intermittence stage. The removal of one or more drops from the end of the point brings the initial discharge voltage nearly up to the value it has after a current has been flowing.

10. The following examples will give an idea of the range of voltages over which the various types of discharge extend. Thus a point with a hemispherical meniscus whose radius was 0.025 cm. gave the first momentary discharge at + 4,000 volts, the next came at 4,110, the next at 4,200, and so in turn others until at 4,700 volts the discharges came continuously. The intermittent stage changed to the steady stage at 5,125 volts. On lowering the voltage the intermittent stage was resumed at 5,000 volts and the current ceased at 4,750 volts. After raising the voltage to 8,500 and then lowering it, the steady stage repeatedly changed to the intermittent at 5,000 volts as at first, but the current now stopped at 4,800 volts. At the transition stage the steady current of 4.9×10^{-8} amperes changed to an intermittent current whose mean value was 5.8×10^{-8} amperes.

With another point having a radius of 0.034 cm. the first discharge was observed at + 4,100 volts, the next at 4,250, and so on until at 5,250 discharges passed continuously about one a second, and at 5,350 the rate had increased to several per second. At 5,750 volts the intermittent current of 9.8×10^{-8} amperes changed to the steady current of 6.2×10^{-8} amperes.

A still larger point of radius, 0.045 cm., gave the first momentary discharge at + 4,500 volts with others in turn as before. The intermittent current changed to the steady form at 6,050 volts. With decreasing potentials the steady current changed back to intermittent at 6,025 which ceased at 5,760.

[1] If the current is diminished very rapidly to zero, it is apt to stop at a higher voltage than is otherwise the case.

In some cases the stopping potentials obtained on different days varied by as much as 3 or 4 per cent., but the condition accountable for this has not been ascertained.

Luminous Appearance.

11. The luminous effects which are seen in a dark room near the end of a liquid point at once decide that the positive discharge is of quite a different character when intermittent from what it is while a steady current is passing. In the latter case, for the larger currents the whole hemispherical surface is covered with a coating of steady purplish light of imperceptible thickness, and with the smallest current at which this form of discharge exists, usually less than half of the hemisphere is covered with the luminous coat.

When the current is intermittent, however, in place of the luminous coat, there is seen at each discharge a fibrous like brush of light which starts from a small area on the liquid surface and reaches out half way to the plane. Near the surface of the liquid, the light is confined to a narrow region and here it is much brighter than in the brush part proper. The general appearance is seen from the drawing *a* in Fig. 2. It appears to be a real positive brush discharge. Just before the intermittent form changes into the steady form the luminous effects of both kinds of discharges are seen at times. They either coexist or there is a rapid succession of changes of one kind into the other.

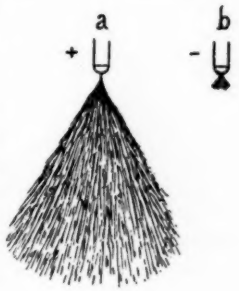

Fig. 2.
Appearance of intermittent positive discharge and of negative discharge.

12. The negative discharge is nearly always an intermittent one (occasionally no intermittence was observed) and in the dark the light from it has the appearance of a short stubby brush. The brush starts from a very small area of the surface and is especially bright at this initial point. Its appearance is shown at *b* in Fig. 2, and it is seen to be a typical negative brush discharge.

Oscillations of Meniscus.

13. The character of the oscillations of the meniscus during the intermittent stage of the discharge has been studied by making observations in light from the spark of a Leyden jar. Drawings of some of the instantaneous outlines, observed in this way during discharge from a point of 0.034 cm. diameter, are shown in Fig. 3.

For the smallest positive currents the oscillations usually are confined to the limits indicated in *a* and *b*, although now and then the form *c* was seen, the pointed top flying off in a drop having a diameter about one tenth of that of the tube. The outlines *d*, *e*, *f*, *g*, *h* and *i* show some of the forms seen with larger positive currents. When the current was

about to change from intermittent to steady, the meniscus showed the agitated appearance indicated in *k*, the meniscus tossing about from side to side and drops of liquid flying off from its end. Without intermittent light this has the appearance *l*, as if the surface were breaking into spray. The contrast is very remarkable when the meniscus of so much commotion suddenly becomes a perfectly still and clear-cut hemisphere as the current changes to the steady form.

14. In the case of the negative discharge the appearance for small currents was much the same as with the positive, forms *a*, *b*, *d* and *e* being seen, but form *c* was not observed. With large currents (many

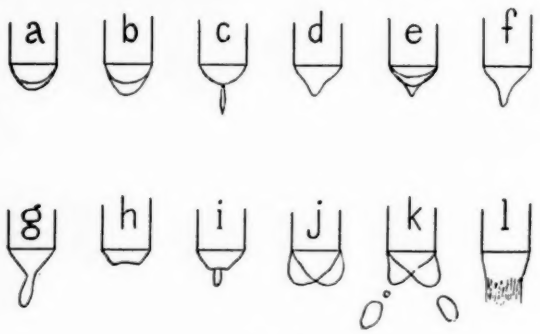

Fig. 3.

Oscillations of meniscus during intermittent discharge.

times larger than the positive ones with which the form *k* was observed) using potentials above 8,000 volts, the meniscus was comparatively steady, although moving about as shown at *j*. Excessive pressure in a meniscus always results in large drops flying off, and it is difficult to know what external pressure should be applied which would make the meniscus hemispherical were it not in motion. Thus with the negative discharge just considered, where the applied pressure remained unchanged throughout, during the range of voltages from 6,000 to 8,000, large drops were thrown off from the meniscus, while this was not the case for lower or higher voltages than these. The conclusion is drawn that with this discharge, the electric intensity at the point, after the current has started to flow, first increases considerably with increase of potential and then falls again to the initial current value or still lower.

15. The oscillations of the meniscus are doubtless attributable to the intermittent character of the discharge, the electric force at the surface being smaller with the current flowing than without a current. The fact that during an intermittent discharge, this is of such a character that it is limited to a very small area on the surface, must produce differences of

surface tension over the surface which help to upset its equilibrium. Changes in surface tension actually occur after the first momentary discharges, as already described.

Electric Intensity at a Discharging Surface.

16. The principle of the method used for measuring the electric intensity has been described in § 7. The difference in level of the liquid surface in *F*, Fig. 1, when the point is at the potential under observation and when uncharged, must be measured, the meniscus at the end of the discharge point being of the same height in both instances.

For the steady positive currents, this pressure can easily be measured. The intermittent stage of the positive discharge is included in a rather short range of voltages and in the lower part of this range also, the pressure can be obtained quite accurately.

When the momentary discharges occur but slowly, it is noticed that just before each discharge the center of the meniscus rises slightly and forms a portion of greater curvature from which the discharge takes place, following which the whole meniscus flattens in the way already described in § 9. A little uncertainty arises from not knowing to just what height the meniscus should be forced in this case. The method adopted was to bring the meniscus to such a point that it rose to the adjusted cross hair (*E*, Fig. 1) at each discharge. However, a slight increase in pressure only was necessary to raise the meniscus from the position named to where it touched the cross hair before the sudden elevation preceding discharge, just noted, took place.

17. The measurement of the pressure within a high meniscus when at zero potential offered two difficulties. The first is the one already mentioned due to the ease with which the meniscus overflowed the sides of the tube. Running the discharge for a time helped matters considerably, unless the scratch on the side (§ 5) was too prominent.

The second difficulty arises from the way the surface tension of the meniscus changes on standing, while no discharge is passing. It was necessary to determine the pressure in the meniscus for zero potential immediately after the discharge was stopped in order that the surface tension might be as nearly as possible of the same value as during the discharge. The pressure thus obtained was usually a little larger than was found with a surface made fresh by the removal of one or more drops. It is possible that ordinarily some impurities collect on the outside of the glass tube and are able to pass gradually to the liquid, whereas the discharge dries this glass surface so thoroughly that it takes time before a layer of moisture, sufficient for permitting the passage of impurities to the meniscus, can form.

In finding the pressures necessary to overcome the mechanical pull on the surface of the meniscus for potentials below that required for a discharge, it was necessary in each case to start with a potential sufficient for a discharge current and after this had been flowing for a short time to reduce the potential to the one for which the pressure was desired. The results of such measurements have been stated already in § 8.

18. An example of the character of the results is shown in Fig. 4, where

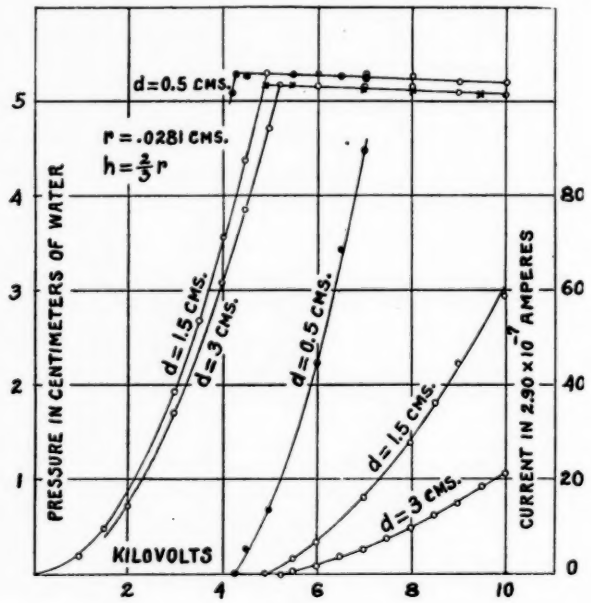

Fig. 4.

Positive discharge currents and liquid pressures required to counteract the mechanical pull of the electric field.

data are given which were obtained for the positive discharge from a point of 0.0281 cm. radius with a meniscus having a height h equal to two thirds of the radius of the tube. The ordinates of the curves starting at the left give diminutions in the water pressures[1] which were required to counteract the electric pull arising from the potentials expressed as abscissas. The curves at the right give the corresponding currents flowing from the points.

Starting at the origin of the right curve which is marked to indicate that the distance, d, between the point and the plane was 1.5 cm., it is seen how the pressure increases along a parabola as long as no discharge passes, but as soon as the starting potential of 4,900 volts is reached, the

[1] For the sake of brevity, these diminutions of pressure will be spoken of simply as the pressures.

curve turns abruptly (follow open circles), and shows now a slight decrease in the water pressure with increase of voltage. This indicates that the electric intensity at the discharging surface for currents of all values is approximately the same as is required to start the discharge. A similar result for platinum points was obtained by Chattock.[1]

19. With a negative discharge, it was not possible to get the water pressures with any accuracy when the current was flowing, owing to the disturbed condition of the meniscus.

As indicated in § 14, however, the electric intensity appears to increase with voltage for a certain range after the discharge begins, and then to decrease again, finally reaching a lower value than was necessary to start the current. Measurements with the negative discharge were confined to the determination of the potentials at which the current started and ceased, and of the electric intensities at the surface which corresponded to these potentials.

The noteworthy result was obtained with all of the points used that the starting and stopping potentials and the surface electric intensities under these conditions were the same for the negative discharge as for the positive. When any differences were observed they were as often in one direction as in the other.

The result is contrary to the prevailing notion of the behavior of the two discharges from metallic points, which is that the negative discharge begins at a considerably lower potential than the positive. This is true for points of a very small diameter but some of the writer's previous results[2] with brass points show that the difference between the starting potentials for the positive and negative discharges becomes less and less as the radius of the discharge point is made larger and larger, until the two become the same when the radius is as large as 0.02 or 0.025 cm. The smallest point used in the present experiments had a radius of 0.0146 cm.

20. Some results obtained with the same point with distances of 0.5 cm. and 3 cm. between the point and plane are also given in Fig. 4. Those for $d = 0.5$ cm. are represented by black circles, the observations having been taken on the same day as those just given for $d = 1.5$ cm. It is seen that although the current begins at a much lower potential in this case (4,200 volts), the pressure in question after the current has started is nevertheless the same for each voltage as when d was 1.5 cm. The currents for corresponding voltages, as shown by the lower curves, are much larger with the shorter distance between point and plane.

The results given in the curves marked $d = 3$ cm. were obtained on a

[1] A. P. Chattock, Phil. Mag., 20, p. 266, 1910.

[2] J. Zeleny, PHYS. REV., 25, 1907. Curves on pages 313 and 324.

different day from the preceding, the atmospheric pressure being less and the temperature higher. Some results obtained on that day with a distance of 1.5 cm. are represented by crosses on the horizontal part of the pressure curve for $d = 3$ cm., and it is seen that the pressures are again identical during the discharge.

These results show that the increase in the volume charge in the gas between the point and the plane almost exactly neutralizes all effect of increase of voltage of the point upon the electric intensity at the discharging surface. Since more ions are produced with the higher voltages this limiting electric intensity must extend farther into the gas, the larger the current. Hovda[1] has shown that in the space between the point and plane the electric force is very nearly proportional to the square root of the current. This proportion evidently does not hold at the discharging surface.

21. The relation between the currents i and the applied voltages V is not expressed well for these points by Warburg's formula,[2]

$$i = aV(V - M),$$

where M is the minimum potential at which a current flows. In most of the cases, M must be given a value larger than the observed minimum potential to make the equation applicable.

To illustrate the effect of changes in the height of the meniscus upon the current flowing from a point, some results are given in Table I. which were obtained with a point of radius 0.0281 cm. The heights of the menisci are expressed as before in terms of the radius of the tube. The numbers show that the shape of the meniscus does not influence greatly the current flowing from the point, for voltages removed considerably from the starting potential, which itself is changed considerably by a change of meniscus.

TABLE I.

Variation of Current with Voltage for Menisci of Different Height.

Height of Meniscus.	Starting Potential.	Currents in 2.9×10^{-7} Amperes.		
		6,000 Volts.	8,000 Volts.	10,000 Volts.
1/3 radius.	4,900 volts.	7.8	29.0	59.9
2/3 "	4,900 "	6.8	27.7	59.0
1 "	4,750 "	7.2	29.3	58.2
2 " [3]	4,200 "	8.0	27.2	56.5

[1] O. Hovda, PHYS. REV., 24, p. 25, 1912.

[2] E. Warburg, Wied. Annalen, 67, p. 69, 1899.

[3] When the current is flowing from its surface, a drop may be drawn out in cylindrical form to an astonishing length.

22. The counteracting pressure during discharge was not found in all cases to be so nearly the same for all values of the current as in the example given in Fig. 4. The observed pressure was found in some cases to increase with voltage and in other cases to decrease, depending upon the height of the meniscus and upon the diameter of the point used. Some variations of this kind are shown in Fig. 5, by the curves giving

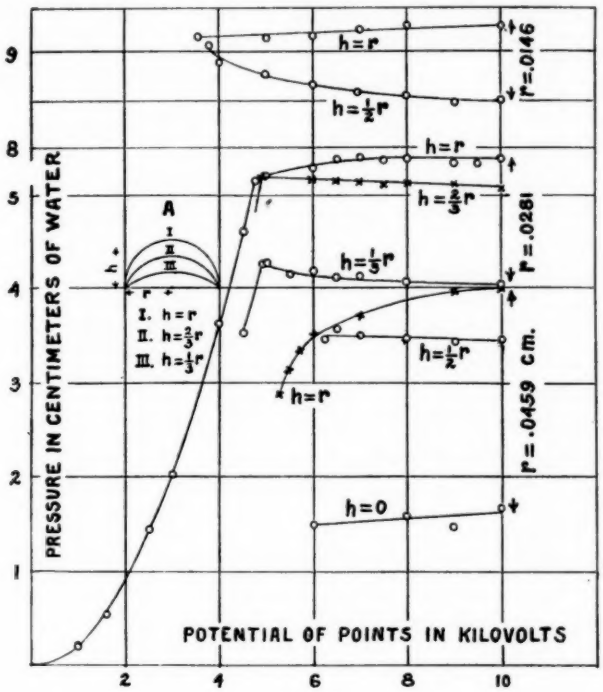

Fig. 5.

Effect of height of meniscus and size of point upon the electric force at the surface.

results obtained with points of three different radii, whose values are indicated on the right side. Two or more heights of meniscus are represented in each case, the height h being given with each curve in term of the radius of the glass tube from which the meniscus protrudes. At A are drawn three menisci of the heights indicated, to picture more clearly the differences. The first reading at the left end of each curve is that corresponding to the voltage required to start the current, except that with the middle point some values are given on the downward slope of the pressure curve preceding the beginning of the current.

Considering first the smallest point, $r = 0.0146$ cm., it is seen that the pressure for the initial current is nearly the same in the two cases given, but while for $h = r$ the pressure increases slightly with increase of

voltage, for $h = \frac{1}{2}r$ on the other hand the pressure diminishes considerably, more especially during the first part of the range.

With the second point, $r = 0.0281$ cm., the initial pressures are alike for $h = r$ and $h = \frac{2}{3}$, and for increasing voltages the values remain nearly alike, increasing somewhat with voltage in the first case and diminishing in the second case. When the meniscus is lowered to $h = \frac{1}{3}r$, the pressures for all of the voltages are smaller by twenty per cent.

In the case of the largest point, $r = 0.0459$, it is to be noted particularly, that with $h = r$ the pressure increases quite rapidly at first with increase of voltage. The curve for $h = \frac{1}{2}r$ starts higher and is nearly horizontal. A curve for a flat meniscus, $h = 0$, is also added, but this is not directly comparable to the others since the discharge here took place from the sharp edge of the tube.

The facts to be noted are that with increasing diameter of point the pressure which overcomes the electric pull diminishes, and that with the smaller points, the pressure where the current starts is almost the same for menisci differing considerably from the hemispherical shape. Since the electric intensities vary as the square roots of the pressures which have been plotted, the ratio differences between the intensities at various voltages or under different conditions are only about half as large as exist between the pressures.

23. In Fig. 6 are plotted pressure-voltage curves for positive discharge from some of the points of different sizes which were used, the height of the meniscus being in each case equal to the radius of the tube. The whole range of sizes used is included, the radius corresponding to each curve being given in centimeters at its right end. The first observation recorded at the left end of each curve represents the voltage at which the discharge stopped and began again. It will be noted that these plots are nearly straight lines for the smaller points, and that they become more curved and show a greater rise in pressure with voltage as their size increases.

Mention should be made of a peculiarity observed at times with some of the smaller points but not shown by any of the curves given. In these cases, as the voltage was increased above the minimum potential, the pressure at first fell rather rapidly by a small amount to the nearly constant value which obtained over a wide range of higher voltages.

The different character of the pressure curves for points of different sizes needs explanation. The difference may arise simply from the fact that with the larger points the meniscus differed considerably from the hemispherical shape at the starting potential and while small currents

only were flowing, although with the larger currents the shape was as nearly hemispherical as the eye could judge. At A, near the bottom of Fig. 6, a curve drawn inside of a semi-circle shows approximately the appearance of the meniscus at the starting potential with large points. This distortion does not exist when the meniscus is not charged and hence acts to give too low a value to the pressures which have been plotted,

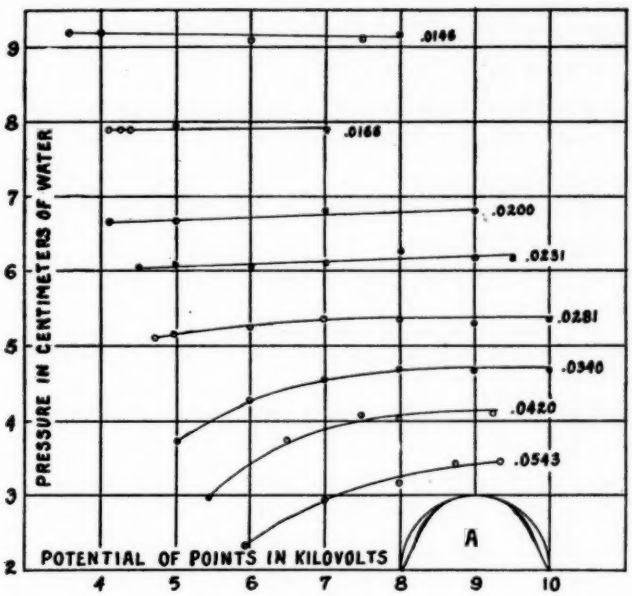

Fig. 6.

Electric intensities at the surfaces of various sized points, during discharge.

since the increased curvature of the surface partly counteracts the electric pull on the surface. The pressure for zero potential with the distorted meniscus might be calculated from the known surface tension by measuring the curvature at the end of the meniscus and from this the true value of the electric pull might be determined. Again it might be assumed, from analogy with the small points, that the pressure at the high voltages where the meniscus is hemispherical is nearly what it would be at the starting potential for a meniscus of the same shape.

With these large points the currents, as indicated by the coating of light on the surface, only spread very gradually to the whole area of the hemisphere, and it is possible that this is the chief reason for the different shapes in these cases of the pressure curves under consideration.

24. An experiment was tried to see if any effect upon the electric intensity at the starting potential could be observed owing to the different

distribution of the electric field when in one case the point is charged and the plane is to earth, which was the usual arrangement, and in the other case where the plane was charged and the point was to the earth. The intensities in the two cases were found identical, notwithstanding the fact that to start the discharge when the plane was charged, the potential required was 1,000 volts higher (r = 0.0146 cm.) than in the other case.

25. In another experiment using a point of radius 0.02 cm., the plane was replaced by a hemispherical cup of 1.5 cm. radius, the end of the point being situated at the center of curvature. The value found for the intensity at initial current was not essentially different from the value obtained with a plane at 1.5 cm. distance, being about 2 per cent. smaller. The hemispherical cup might be used to advantage with large points as the field would tend to keep the menisci more hemispherical.

26. If the glass of which the tube is made were to act as a perfect insulator, the conducting portion of the point would consist of the liquid cylinder, expanding at the end into a hemisphere of considerably greater radius. The distribution of the field at the end of such a conductor would naturally be different from that obtaining where the material of the tube is conducting. Two tubes, having radii 0.045 cm. and 0.0185 cm. were therefore silvered on the outside and the value of the electric intensity determined at the surface of the liquid hemisphere for each, at the starting potential. The values found were identical with those obtained before the points were silvered, indicating that the clean glass surface either by conduction or from ions in the gas, gets the same surface charge a conductor would have.

27. The method used for measuring the electric intensity presupposes that the surface tension of the liquid has the same value when the two measurements of pressure are being made, *i. e.*, while the current is flowing from the surface and when the surface is uncharged. In the former case, it is possible that the current heats the surface sufficiently to change its surface tension by an amount that should be taken into consideration. To test this point a thermal couple made of very thin wires was introduced into the liquid of the meniscus by running the wires into the inside of the tube at the rubber connection, shown at B, Fig. 1. The apparatus was now used with the plate charged and the point to earth, and it was found that even with the largest currents which had been employed in these experiments, the temperature of the drop of liquid was changed by only about 2° C. Moreover, the temperature was diminished by the current, owing, no doubt, to an increase in the rate of evaporation. When the meniscus was lowered so that the wires

of the thermal couple protruded from the liquid and the discharge started from them, an increase of temperature of about the same magnitude was observed. This last is in agreement with some of the writer's former experiments.[1]

That some slight differences in surface tension over the surface of the meniscus exist during discharge is indicated by the circulation inside of the liquid of any small specks of solid matter that may happen to be there.

28. The effect of the gamma and beta rays from radium upon the starting potentials of several points was tested by bringing up a glass tube containing a little over 3 mg. of radium to within 4 cm. of the points. In a few cases this produced a change which amounted to a lowering of the starting potential by about 25 volts, this being the smallest change detectable with the voltmeter used. In such cases if the potential was reduced very slightly below the stopping potential while the radium was not in place, bringing up the radium caused a very small current to start which disappeared again on removal of the radium.

With metal points, the surface conditions cause a retardation of the starting potential so that when the current does start, it jumps at once to a value which is considerably larger than the smallest currents detectible in these experiments. The effect of radiations on such points is to reduce this retardation of the starting potential and make this latter coincide with the stopping potential, as Warburg and Gorton (loc. cit.) have shown. For these liquid points the current while beginning with an intermittent stage nevertheless starts very much more gradually than it does with the metal points, so that the same conditions are not present to be influenced by the radiation. The effect of more powerful ionizing agents which have been studied in some detail, is very pronounced but this will be considered in another paper.

29. The value of the electric intensity at the surface of the liquid when a positive current just ceases to flow from it was determined about ninety times all told with more than a dozen points ranging in radius from 0.0146 cm. to 0.0543 cm. Many of these determinations were made incidentally while other matters were under investigation, hence they are very unevenly distributed among the points used.

A summary of the results is given in Table II.

Column 1 gives the radii in centimeters, and column 2, the number of the determinations of the electric intensity f, the average of which is given in column 3 expressed in electrostatic units per centimeter. The individual results for f obtained with any point differ in but one or two

[1] Proc. Royal Soc. London, 82, 1909. Note to paper by Barnes and Shaw.

TABLE II.

Electric Intensity at Discharging Surface.

1	2	3	4	5	6	
r	n	f (water)	$f\sqrt{r}$	T	f (brass)	
					+	−
0.0146 cm.	21	471	56.8	73.8	508	482
.0166	3	436	56.2	68.5	474	.....
.0178	3	416	55.5	69.0	443	430
.0185	3	414	56.3	70.7	435	.....
.0200	18	405	57.2	70.5	415	409
.0229	13	382	57.8	72.8	390	.....
.0250	6	353	55.8	66.2	374	376
.0281	1	356	59.7	.....	351	.....
.0340	10	309	57.0	72.6	318	.....
.0370	1	294	56.6	71.2	304	.....
.0419	4	270	55.3	76.0	285	.....
.0451	4	276	58.6	73.7	275	.....
.0543	3	241	56.2	79.0	250	.....
Average....	.....	.....	56.9	72.0	.....	.....

cases by more than two per cent. from the mean value given. The barometric pressure was usually close to 74 cm. of mercury with a maximum variation from this of about 5 mm. The temperature during most of the observations was about 22° C., although the extremes were 20° and 26°.

It is seen that the value of f for the smallest point is about twice that for the largest point. The results can be represented very well by the empirical relation $f\sqrt{r}$ = a constant. The values of this product are given in column 4, the average being 56.9.[1] There are no systematic variations in column 4 from this value, and the larger deviations which exist may be attributed to the lack of perfection in the ends of the points.

It must be remembered however that the considerations given in § 23 raise the question whether the values obtained for the electric intensity with the larger points are not really too low.

30. Column 5 in Table II. gives the values obtained by the method described in § 6 for the surface tension T of the liquid used (water very slightly acidulated with hydrochloric acid). The average of the values given for all of the points is 72.0. By the capillary tube method, the surface tension of the same solution was found to be 71.3.

The larger deviations from the true value are an indication of the

[1] Combining this relation with the equations in §§ 6 and 7 it can be shown that $p = 9/10\ h$ nearly. This means that at the potential for which a current starts the liquid surface in F (Fig. 1) is always situated a small distance only above the level of the discharge point.

difficulty experienced in some cases of getting the true pressure owing to the readiness with which the liquid overflowed the sides when not charged, but in some cases they arise from the meniscus being somewhat distorted because of the unevenness of the edge of the glass tube. A distortion of the kind just mentioned, while it would result in giving an incorrect value of the surface tension, would not affect the determination of the electric intensity if it did not change its character with the charging of the liquid.

31. Chattock[1] found the relation $f.r^{0.45} = 85$ to represent his determinations of the electric intensity at the surfaces of platinum points when a positive current just ceased to flow. The size of the points used is not stated, but his formula when applied to the extreme limits of size used in the present experiments gives values over 20 and 30 per cent. larger respectively for the smallest and largest points. Whether this difference between the results with water and platinum surfaces is a real one arising from some inherent difference in the two kinds of surfaces or whether it is to be ascribed to some inaccuracy in one or the other of the methods used in making the measurements, remains to be determined.

Some of the results obtained by the writer[2] for the minimum potentials of brass points of various sizes were gotten under like conditions to those obtaining in the present experiments, except that the point was situated in a metal vessel. The method explained in § 8 should therefore be applicable to those results and the electric intensity at the surface of the cylindrical brass points with hemispherical ends may be calculated from the minimum potentials. Values of f thus computed from the results taken from Figs. 2 and 5 of the paper cited, are given in column 6 of Table II. The values for the brass points are on the whole several per cent. larger than for the water points, the divergence being largest for the smallest points.

Preferable to computing the electric intensities for the brass points, a more direct method of comparing the behavior of the two kinds of points would have been to compare the values of the minimum potentials. This is not done because the determinations of the minimum potentials with the liquid points show some peculiarities not fully understood. Thus the value obtained might be different by over a hundred volts on some occasions without any similar change in the electric intensity. This much may be said of the potentials obtained, and this should be contrasted with the relative values of the electric intensities given above, that for the lower half of the range of sizes used the minimum potentials

[1] A. P. Chattock, Phil. Mag., 20, p. 266, 1910.

[2] J. Zeleny, PHYS. REV., 25, p. 305, 1907.

for the liquid points are almost the same as for the brass points, being a little higher in a few cases, but for the largest points used the minimum potentials are about six to seven per cent. lower.

32. Any discussion of the results which have been presented in this paper will be postponed until the results of some other experiments which have been completed are published. These further experiments deal with the discharge from various kinds of liquid surfaces; with the discharge in different gases at various pressures; and with the effect of intense X-rays and alpha rays upon the discharge from both liquid and metal points.

SUMMARY.

33. The electrical discharge from points whose discharging surfaces consist of slightly acidulated water when placed opposite a metal plate have been studied. The positive discharge was found to begin with a momentary current, which was repeated only by an increase in the potential of the point. At higher potentials the discharge current is intermittent and this is followed by a steady current at still higher potentials. In the last case the liquid meniscus is quiescent and the luminosity covers the surface and is confined to its immediate neighborhood.

With the intermittent form of positive discharge the liquid meniscus is agitated and the light starts from a small area on the surface and extends half way to the plate in the arrangement used.

The negative discharge is always in the form of a brush discharge and the current is almost always intermittent and the meniscus in motion. The light in this case, however, while starting from a small area of the surface also, extends out into the gas a distance which is only about equal to the diameter of the point.

The momentary discharges, which first take place from the liquid surface, produce some effects there which result in an increase in the surface tension. This arises, most likely, from the surface being cleansed of some material collected there. It is probable that some such effect is likewise produced when metal surfaces are used.

A hydrostatic method is given for measuring the electric intensity at the surface of liquid points both before and during discharge. The surface tension of the liquid may also be obtained with the same apparatus. The product of the electric intensity at the discharging surface when a current just ceases to flow by the square root of the radius of the point, was found to be a constant equal to 56.9. The radii of the points used range from 0.0146 to 0.0543 cm.

The electric force under these conditions, as well as the potentials at which the currents cease to flow, were found to be the same for the negative and for the positive discharges.

For the small points of the range given the electric intensity at the surface of a hemispherical meniscus, when a current of any magnitude is flowing, is nearly the same as at the minimum potential, but for the larger points the value increases with current, becoming nearly constant at higher values of the latter.

The electric force at the surface of the smaller points used was influenced to a small extent only by changing the height of the liquid meniscus considerably from the hemispherical form. This intensity was not affected by such changes in the distribution of the electric field as are brought about by changing the distance between the point and plane or by using a hemispherical electrode in place of the plane, or by charging the plane instead of the point itself.

With potentials considerably above the minimum value, the current flowing from a given point was found to vary but slightly when the height of the meniscus was changed greatly.

The temperature of the liquid of the meniscus during the discharge was measured and found to be slightly lower than it was while no discharge was passing.

Results were obtained which permit the calculation of the electric force under certain conditions at the surface of a point while no discharge current is passing.

The action of the beta and gamma rays from three milligrams of radium was found to lower slightly the starting potential.

The values obtained for the electric intensity at the minimum potential with liquid points are considerably smaller than those obtained by Chattock with platinum points and somewhat smaller than those calculated by the writer from some of his measurements on brass points.

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December 19, 1913.

NOTES ON QUANTUM THEORY.

A THEORY OF ULTIMATE RATIONAL UNITS; NUMERICAL RELATIONS BETWEEN ELEMENTARY CHARGE, WIRKUNGSQUANTUM, CONSTANT OF STEFAN'S LAW.

BY GILBERT N. LEWIS AND ELLIOT Q. ADAMS.

THE importance to science of a simple and established set of units has led to the almost universal adoption of the system based upon the centimeter, the gram and the second. These units themselves, however, have no rational significance. The centimeter was intended to be a certain simple fraction of the earth's circumference; the gram to be the weight of one cubic centimeter of water at the temperature of its maximum density, and the second is a certain fraction of the mean solar day. But neither the size of the earth nor its velocity of rotation is unique or even constant; nor does water in any notable way stand by itself among substances.

It has sometimes been assumed that there is some peculiar appropriateness in choosing three and only three fundamental units. This is by no means the case. It happens that the branch of physics which was first developed was the mechanics of rigid bodies. That science may be represented by a manifold of five dimensions, in which the three dimensions of space, one of time and one of mass,—or density,—are the five independent variables. In general for the treatment of such a manifold, five fundamental units would be necessary, but owing to the symmetry of the space of Euclidean geometry it is possible and convenient to adopt a single unit—that of length—in the discussion of all problems in three-dimensional geometry. The number of units required by the mechanics of rigid bodies is thus reduced to three. When, however, we consider other branches of physics, other units are necessary. Thus in the theory of heat it is customary to introduce new units, such as the unit of temperature, without attempting in the first instance to determine the dimensions of these units in terms of the units of mechanics. On the other hand, when important relations between existing units are discovered, the number of units which are to be regarded as fundamental is reduced, as we have pointed out in the case of the units of geometry.

Since it was, in fact, in the science of geometry that such a reduction in the number of fundamental units first occurred, it may be well to consider in this simple case the nature of the assumptions made.

In the first place, owing to the existence of rigid and movable measures of length, it was assumed that distances in all directions can be expressed in terms of a common measure. But fixing the unit of length does not determine immediately the unit of area, or of volume. The units actually chosen are the area of a square of unit side and the volume of a cube of unit edge, but many different units might have been proposed. Unit area might have been defined as the area of a circle of unit radius, or diameter, or circumference.[1] These units would be to the one actually chosen in the ratios π, $\pi/4$ and $1/4\pi$ respectively. There are numerous reasons for preferring the units actually in use, not the least important of which is the fact that an area or volume may be built up of squares or cubes, but not of circles or spheres. Admitting, then, that the choice is a wise one, it must nevertheless be emphasized that it is a choice of a somewhat arbitrary character.

Having made this choice, however, it is important to make a similar choice wherever a similar occasion arises, and thus to adopt consistently a system of "square" units.[2] In the case of angles the choice of unit has not been unanimous. In one system a simple fraction or multiple of a right angle is the unit, in the other the unit is the angle subtended by a circular arc equal to the radius of the circle and in this latter system a right angle is $\pi/2$. In our sense we shall speak of the former unit as a "square" unit just as the latter is commonly known as the "circular." We shall have occasion to notice how frequently the choice between two fundamental units involves the introduction or omission of some simple function of π.

When we add to the three dimensions of space the one dimension of time we obtain the four-dimensional manifold of kinematics. The science of kinematics involves geometry and a further degree of extension in time. Kinematics, therefore, in the broadest sense, includes all of

[1] The second of these units is actually in use in stating the cross section of circular wire, which is said to be one circular mil when the diameter is one mil.

[2] We might make an even more fundamental classification, for the axioms and propositions of geometry may be divided into those which depend upon parallel translation and those which depend upon rotation [cf. Wilson and Lewis, "The Space-Time Manifold of Relativity," Proc. Amer. Acad., *48*, 389 (1912)]. The parallel geometry is more general and is common to Euclidean geometry and to the non-Euclidean geometry of relativity. In this parallel geometry we may divide a given plane into unit parallelograms, and such conceptions as density can be readily introduced; but a field possessing radial symmetry about a point could not be adequately treated. For the most part, the square units we shall adopt will be identical as far as this is possible with those which could be obtained from the parallel geometry alone.

Euclidean geometry as a special case. In other words, geometry may be regarded as a cross-section of zero extension in time, through the manifold of kinematics.

In classical kinematics the units of length and of time were regarded as independent. The first great step toward the realization of the essential interdependence of these two units was made by Maxwell when he discovered the identity between the velocity of light and the ratio of the electromagnetic to the electrostatic units. Maxwell inferred that this identity was merely an evidence of the electromagnetic nature of light, but the development of the principle of relativity has led us to a more fundamental conclusion, which perhaps can best be stated in the following form: The constant c, known as the velocity of light, is merely a number imposed upon kinematics through the arbitrary choice of the centimeter and the second as units of length and time. In other words, all the equations of physics may be simplified by choosing a unit of time which is to the second in the ratio of 1 to 3×10^{10}. As examples we may cite the Maxwell equations of electricity and magnetism or the equation for the pressure of a beam of light in terms of the energy emitted or received per second, or any of the equations of non-Newtonian mechanics, in all of which cases every term which has the dimensions of time to any power contains the factor c to that power.

Not only has the principle of relativity shown the existence of this relation between the fundamental units of time and space, but it has enabled us to construct for kinematics a four-dimensional geometry which is as satisfactory as the Euclidean geometry of ordinary space. "Suppose that a student of ordinary space, habituated to the interpretation of geometry with the aid of a definite horizontal plane and vertical axis, should suddenly discover that all the essential geometrical properties of interest to him could be expressed by reference to a new plane, inclined to the horizontal, and a new axis inclined to the vertical. Whereas formerly he had attributed special significance to heights on the one hand and to horizontal extension on the other, he would now recognize that these were purely conventional and that the fundamental properties were those such as distance and angle, which remain invariant in the change to a new system of reference."[1]

In the four-dimensional geometry of kinematics an interval of time is a length, and we have the same reason for adopting a single fundamental unit in kinematics as in geometry. We shall use the centimeter provisionally as this unit. The dimensions of any kinematic quantity must therefore be represented by a power of a single dimension. This di-

[1] Wilson and Lewis, l. c.

mension, representing a one-dimensional interval in space or in time, will be denoted by $[I]$. Thus the dimensions of area are $[I]^2$, of volume $[I]^3$; both angle and velocity have zero dimensions; acceleration is $[I]^{-1}$, angular velocity $[I]^{-1}$ and angular acceleration $[I]^{-2}$.

Of the secondary units of kinematics the most important is that of velocity and there can be no dispute as to the desirability of choosing in this system the velocity of light as the unit of velocity, every other velocity is therefore a proper fraction, but in the case of other secondary units the choice is not always obvious. Thus the unit of angular velocity to be chosen depends upon the previous choice of unit angle.

In mechanics a new variable appears, and the choice of mass, energy, density, force, momentum, or any other simple mechanical quantity to serve as this new variable is quite arbitrary. Since it is customary we will regard mass as this primary variable and take, provisionally, the unit of mass, the gram, as independent of the unit of kinematics. All mechanical quantities may therefore be assigned dimensions in terms of interval $[I]$ and mass $[M]$. Thus energy and momentum have the dimensions $[M]$, force is $[M][I]^{-1}$; density and pressure $[M][I]^{-3}$, etc. The secondary units which have been universally adopted for these quantities seem to be unquestionably the best. In our system the gram is the unit of momentum and of energy as well as of mass, and the unit of force is one gram per unit interval, which may be derived from any of the older expressions for force, namely, energy per unit distance, momentum per unit time, or mass times acceleration.

The theory of heat involves at least one new variable. Since the discovery of the "mechanical equivalent of heat" the dimensions of thermal quantities can be expressed in terms of mechanical dimensions and of temperature. Thus it is customary to regard entropy and "heat capacity" as having the dimensions of energy divided by temperature. If now in addition to the "mechanical equivalent of heat" we find another very fundamental relation between thermal and mechanical quantities we shall be justified in eliminating temperature as a fundamental dimension. Such a relation is in fact furnished by the constant of the gas law, a law which is valid for all substances in the gaseous state at a sufficient degree of attenuation. This equation is ordinarily written: $PV = nRT$, where n is the number of mols. Since R is a universal constant we could, by using in place of the Centigrade degree a unit R times as small, simplify the formula to $PV = nT$. Since, however, the molecule seems a more desirable unit than the mol, and since the number of molecules, N, in one mol is now known about as accurately as the molecular weights, we will write for the number of molecules in n mols

$m = nN$, and the gas law becomes $PV = m(R/N)T = mkT$, where k is another universal constant. Now this constant appears not only in the equation for gases, but also in other important formulæ, and always to the same power as T, for example in the so-called Rayleigh equation for the distribution of energy in black radiation, $E_\lambda = c\lambda^{-4}kT$. We may therefore eliminate this constant once for all by writing $\theta = kT$, where the unit of θ is k times the Centigrade degree. The gas law becomes $PV = m\theta$. Any dimensions which k may have possessed are now incorporated in the temperature θ, and temperature therefore has the dimensions of energy or mass.

This process of reducing the number of fundamental units, or dimensions, which has been proposed only recently[1] for the thermal quantities, was adopted at the outset in the case of electrical quantities. If in the first instance electric charge had been measured in some arbitrary unit, then Coulomb's law would have contained a universal constant, like c or k. Charges were, however, so defined as to make this constant unity, and on the assumption that it is also free from dimensions the electrostatic system of units was developed. Another important system of units, the electromagnetic, becomes identical with the electrostatic when we take the velocity of light as unity. The adoption of the electrostatic system led to a number of equations in which the prominence of the factor π led Heaviside to suggest another unit of charge which is to the former as $1 : \sqrt{4\pi}$ and which Heaviside called the rational unit. The difference between the electrostatic and the Heaviside units is like the difference between the circular and square units of area; Coulomb's law expresses the force between two charges, each of which determines a field of radial symmetry while the Heaviside unit is so chosen that the capacity of a unit cubical condenser is unity.

In the preceding discussion of the methods by which geometrical, kinematical, mechanical, thermal and electrical quantities may be expressed in terms of a few fundamental dimensions or units, we have attempted to point out the difficulties attending the choice of secondary or derived units, but also to indicate, in spite of these difficulties, the way in which we may hope to diminish still further the number of fundamental independent dimensions. Having expressed all of the quantities hitherto considered in terms of two arbitrary units of interval and mass, it is necessary only to find *one* more relation of a universal

[1] Planck, Vorlesungen über die Theorie der Wärmestrahlung. First edition, p. 164. We should call attention here to the fact that Planck has suggested a system of units from which the arbitrariness of the ordinary units has been eliminated by the use of a sufficient number of universal constants. Planck did not, however, attempt to make his units rational in the sense in which we use the term.

character in order to express one of these units in terms of the other, or *two* more such relations to determine absolutely both of these units. We shall then have a system of units all of which are in a sense dimensionless. An interesting question now arises. Supposing that instead of finding two such, we found three or more such relations, would we not then have several different sets of rational units between which the choice would be purely arbitrary? Our answer to the question can best be expressed by stating our belief that these different sets of units will be dependent upon one another in a very simple way, and that if in the manner suggested we obtain the ultimate units of interval and of mass by the aid of two universal and fundamental relations, then all universal constants will prove to be pure numbers, involving only integral numbers and π, just as we have seen that in geometry several different units of angle, area and volume may be chosen, which, however, differ only by such a factor. This we shall call the *theory of ultimate rational units.*

There are a number of important constants from which to choose the two which are to determine the ultimate units: the constant of gravitation, the charge of one electron, the mass of an isolated electron, the constant of Stefan's law, the constant h of the Planck radiation equation, and several others which may posses universal significance. Indeed, the properties of any other atom are as universal, presumably, as those of the electron, but in the present state of our knowledge the electron appears to be unique in a sense in which the other atoms are not. Thus if it were decided to choose the mass of some atom as unit mass the mass of the electron would be the most promising choice. While each atom has a different mass, there is however one property of the electron which is in every sense unique, and that is its charge. Unlike the mass of the electron, the charge of the electron is constant under all circumstances. Because of these facts, and because of the success which has attended the various attempts to regard other branches of physics as parts of the science of electricity, we have without hesitation decided to take the electron charge as the first of the two fundamental constants needed for the final determination of the ultimate units.

The dimensions of electric charge become in our system $[M]^{\frac{1}{2}}[I]^{\frac{1}{2}}$ and it is interesting to note that two of the other constants mentioned above have, as dimensions, powers of the dimensions of electric charge, for Planck's h has the dimensions $[M][I]$ and the constant a of Stefan's Law, $[M]^{-3}[I]^{-3}$. We must expect, therefore, that the square of the electron charge, Planck's h, and the reciprocal cube root of a, will differ only by simple numerical factors.

The charge of one electron in ordinary electrostatic units we may call ϵ.

If we call the same charge in Heaviside electrostatic units ϵ', then $\epsilon' = \sqrt{4\pi}\epsilon$. Numerous other systems of electrical units might be invented, and we shall refer to one other in which the electron charge is $\epsilon'' = 4\pi\epsilon$, and which has advantages in certain cases. For example, the energy emitted per second by a simple harmonic oscillator, which has played so large a part in the modern theory of radiation, is in the three units, repectively

$$-\frac{dE}{dt} = \frac{8\pi^2}{3}\frac{E}{M}\epsilon^2\nu^2 = \frac{2\pi}{3}\frac{E}{M}\epsilon'^2\nu^2 = \frac{1}{6}\frac{E}{M}\epsilon''^2\nu^2,$$

where E is the energy, M the mass, and ϵ the charge of the oscillator of frequency ν. Our opinion as to the relative desirability of these units may be modified as the properties of the electron become better understood. Formerly, when electricity was regarded as a continuum, the Heaviside system was unquestionably superior. We have seen that in geometry the unit square is a more satisfactory measure of area than the unit circle, and that in general we must attempt to choose consistently units similar to the unit square and the unit cube. Thus we regard a uniform vector field as simpler than one which possesses radial, that is to say spherical, symmetry. The Heaviside system was based upon the properties of the uniform electric field between the plates of an infinite plane condenser. Whether our present recognition of the atomic nature of electricity deprives the Heaviside system of its advantages is a question which merits the most careful scrutiny.

As ordinarily expressed the dimensions of ϵ^2 are energy times length. According to the choice of the electrical unit it will be natural to choose ϵ^2, $4\pi\epsilon^2$ or $(4\pi\epsilon)^2$ as the unit of energy times interval with the dimensions $[M][I]$. For convenience in the following calculation we shall continue to express the energy in ergs. In terms of this unit we shall expect to find the constants a and h to be simple numbers.

Let us consider first the constant a of Stefan's law, which reads

$$E = aVT^4,$$

where E is the energy (ergs) in the volume V (c.c.) at the absolute temperature T (deg. Cent.). We may put this equation in the form

$$E = ak^{-4}V(kT)^4 = ak^{-4}V\theta^4. \qquad (1)$$

Both E and θ are now expressed in ergs.

Hence $a = k^4(E/V\theta^4)$, where the quantity in parenthesis is measured in reciprocal (erg cm.)^3. If we choose now a new unit of energy times length, namely, ϵ^2, ϵ'^2 or ϵ''^2, we may express the factor in parenthesis in these units by writing:

$$a = \frac{k^4}{\epsilon^6}\left(\frac{E\epsilon^6}{V\theta^4}\right) = \frac{k^4}{\epsilon'^6}\left(\frac{E\epsilon'^6}{V\theta^4}\right) = \frac{k^4}{\epsilon''^6}\left(\frac{E\epsilon''^6}{V\theta^4}\right). \quad (2)$$

And we may expect to find that the three quantities in parenthesis are simple numbers. In fact, it will be seen presently that the third of these numbers is unity, that is,

$$\frac{a\epsilon''^6}{k^4} = \frac{a(4\pi\epsilon)^6}{k^4} = \frac{E\epsilon''^6}{V\theta^4} = 1. \quad (3)$$

The constant a cannot involve π except in so far as this factor is introduced in the unit of energy times length, and therefore only as π^{3p} where p is an integer. The reason for this statement lies in the uniformity of distribution of energy in the hohlraum. There is nothing in the nature of the problem to require the use of any but square units. If Stefan's law were expressed in some other form, for example, if we should write $dE/dt = bT^4$, where dE/dT is the rate of emission of energy from a black sphere of unit radius at the temperature T, b, like a, would be a universal constant, but would contain intrinsically the factor π, since it involves quantities which cannot be completely expressed in square measure. While the constant a therefore does not contain intrinsically the factor π, it might obviously contain some simple coefficient such as 2 or 3/4. This is a more difficult question, but we shall attempt presently from *a priori* considerations to show that no such coefficient is to be expected in the constant a. Meanwhile this will be regarded as an empirical fact on the basis of the following calculations.

The results of numerous experimental determinations of the constant of Stefan's law are extraordinarily discordant. Without considering the earlier measurements, the following results have been published during the last two years for the value of $\sigma \times 10^5$ (where $\sigma = ac/4$): 5.67,[1] 5.80,[2] 5.45,[3] 5.96,[4] 5.54,[5] 5.89,[6] 6.33.[7] The mean of all these values is 5.81, or 5.72 excluding the incomprehensibly high value of Féry and Drecq. Coblentz[8] after a very careful and critical survey of the various determinations gives as the probable value 5.7.

Let us now calculate the value of σ from our assumption (equation 3) that $a = k^4/\epsilon''^6 = k^4/(4\pi\epsilon)^6$. The recent determination of the elementary

[1] Shakespear, Proc. Roy. Soc., *A 86*, 180 (1912).
[2] Gerlach, Ann. d. Phys., *38*, 1 (1912).
[3] Kurlbaum, Verh. d. phys. Gesell., *14*, 576 (1912) (recalculated from older result).
[4] Puccianti, Nuov. Cim., *4* (6), 31 (1912). See also Nuov. Cim., *4* (6), 322 (1912).
[5] Westphal, Verh. d. phys. Gesell., *14*, 987 (1912).
[6] Keene, Proc. Roy. Soc., *A 88*, 49 (1913).
[7] Féry and Drecq, Journ. de Phys. (5), *3*, 380 (1913).
[8] Coblentz, Jahrb. d. Radioakt., *10*, 340 (1913).

charge by Millikan[1] for which he claims an accuracy of 0.2 per cent., a claim which seems to be warranted by the extreme care of his measurements, give $\epsilon = 4.774 \times 10^{-10}$. From the value of ϵ, k can be obtained at once from the equation $k = R\epsilon/F$, where F is the Faraday equivalent in the same units as ϵ. Hence $k = 1.372 \times 10^{-16}$, and since R and F are known with a very high degree of accuracy, the percentage error in k is the same as in ϵ. We thus find $a = 7.60 \times 10^{-15}$ in which the percentage error is twice that in ϵ, as is obvious if we write $a = R^4/(4\pi)^6\epsilon^2F^4$. From this value of a we find $\sigma = 5.70 \times 10^{-5}$.

We believe that the value of a thus obtained is the true constant of Stefan's law, subject only to such uncertainties as are due to the experimental errors in R, F and ϵ.

This result may be presented in a different way. If the equation of the perfect gas be written in the form $PV = m\theta$ and Stefan's law in the form $E = V\theta^4$, these two equations suffice to determine the value of a unit of energy times length, and this unit would then prove to be, within the limits of experimental error, equal to the unit which we have called ϵ'^2. It may be asked why the coefficient of the energy equation representing Stefan's law should be simpler than the coefficient of the corresponding entropy equation, $S = \beta V\theta^3$, where S is the entropy of a hohlraum of volume V at temperature θ, and β is another universal constant, namely $\beta = 4a/3$. Why, then, should we expect a to be unity rather than β? In the units we have chosen, the energy of a unit volume of a hohlraum at unit temperature is equal to two thirds of the energy of one molecule (possessing three degrees of freedom), of any perfect gas at unit temperature. No statement of similar simplicity can be made with respect to the entropy of the hohlraum and that of a molecule. While the average energy at a given temperature is the same for all molecules, and independent of all other conditions, the average entropy of a molecule depends upon the concentration and the chemical nature of the molecule as well. For this reason we should expect a simplicity in the energy equations which the entropy equations do not possess.

We may next proceed to a discussion of the constant h, which appears in the Planck equation for the distribution of energy in the spectrum of a black body, and which must appear in any radiation formula of which the Wien equation is a limiting case. If the Wien equation is in fact true in the limit, the constant h, the "Wirkungsquantum," must be a significant universal constant, irrespective of the validity of any more general expression, such as that of Planck.

If the Planck equation is correct it is possible to calculate h directly

[1] Millikan, PHYS. REV. (2), 2, 79 (1913).

from a, by means of the equation obtained by integrating the Planck equation:

$$a = \frac{8\pi^5 k^4}{15c^3h^3}. \tag{4}$$

If, now, we write, as before,

$$a = \frac{k^4}{\epsilon''^6}$$

then $15c^3h^3 = 8\pi^5\epsilon''^6$, or

$$h = \frac{\epsilon''^2}{c}\sqrt[3]{\frac{8\pi^5}{15}} \tag{5}$$

and substituting we find $h = 6.56 \times 10^{-27}$.

Now the constant of the Wien equation, $c_2 = ch/k$ has been determined with considerable accuracy. The latest value obtained by Coblentz[1] as the mean of several determinations in the Bureau of Standards at Washington is 1.4456 ± .0004, while Warburg, Leithäuser, Hupka and Müller[2] in the Reichsanstalt at Berlin obtain as a mean 1.437 ± .004. The value of c_2 calculated from h as given above is 1.434.

If one admits that the Planck formula is correct, the close agreement between this value and those obtained experimentally affords strong evidence of the correctness of our calculation of the constant of Stefan's law. On the other hand the agreement does not demonstrate the validity of the Planck formula. Numerous substitutes for that formula might be suggested which would agree equally well with the experimental facts and which would not only satisfy the Wien displacement law, but also approach at the two limits the Wien and the Rayleigh radiation formulæ. Indeed it seems hardly likely that if h is a quantity of really fundamental significance it is represented by so complicated a formula as (5).

We hope to revert to this question of the true radiation formula and the significance of the constant h, in a later publication. At present it need only be pointed out that the fundamental quantum in the theory of electricity and of radiation is the quantum of electricity, and that the so-called "Wirkungsquantum" is merely the square of this fundamental quantum with a simple numerical coefficient, depending upon the units chosen.

We shall not attempt at this point to decide finally as to the choice of the ultimate rational units, but the two experimental data by which these units will be determined will be the charge of the electron and the mass of the isolated electron. It is to be hoped that a further study of

[1] Jahrb. d. Radioakt., *10*, 340 (1913).

[2] Ber. Berl. Akad., *2*, 35 (1913).

the law of gravitation will soon enable us to obtain the constant of that law in terms of the chosen ultimate units, as a pure number.

We have attempted in this paper to show the relation between the so-called fundamental and derived units of geometry and physics, and have outlined a theory of ultimate rational units in accordance with which we have obtained relations between several important universal constants. In particular we have derived from this theory a value for the constant of Stefan's law which we believe to be far more accurate than any of the values of this quantity obtained by direct experiment. We have shown that the fundamental quantum in physics is the charge of the electron.

In a following paper we shall attempt to show that the numerous theories of the so-called energy quantum which have recently been advanced are unnecessary for the explanation of the phenomena with which they deal.

CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA,
November 13, 1913.

DISCHARGE IN A MAGNETIC FIELD.

By Robert F. Earhart.

SIR J. J. THOMSON, in the "Discharge of Electricity through Gases" discusses the motion of an ion in a magnetic field.[1] Among the special cases treated is the one where the ion moves in the direction of the magnetic field. The forces are such as to cause a charged particle to travel along a helical path. In a later chapter (pp. 575–579) a résumé of experimental work on the effect of a magnetic field upon a discharge is given. Birkland[2] found that when a discharge tube was placed in a magnetic field and oriented so that the direction of the field coincided with the line joining the electrodes, the potential required to produce the discharge was lowered.

Almy in 1901[3] made a more careful and quantitative study of the case. His experiments were conducted at low pressures and he too found the action of a longitudinal field lowered the discharge potential. Among other things he noted that when the field was applied, the discharge was for the most part concentrated along limited paths and instead of the glow filling the entire tube it was concentrated into stream-like lines.

Willows[4] extended the experiments with some variations and operated with transverse fields as well.

Paalzow and Neeson[5] made some experiments with a tube in the shape of a Greek cross. There were four electrodes pointing toward the intersection of the cross arms. This was placed in a magnetic field in such a manner that the field could be made parallel or at right angles to the electric force. The electrodes consisted of pointed wires, and from their description neither the electric field nor the magnetic field was uniform. They established several interesting points, among others the fact that at some pressures a weak field facilitates the discharge while stronger fields diminish the discharge. The diminution of current strength or increase as the case may be is given in terms of scale divisions of the galvanometer employed. There is a description of the magnet used to

[1] Second edition, pp. 111–116.
[2] Comp. Rendus, CXXVI., p. 586, 1898.
[3] Proc. Cam. Phil. Soc., XI., p. 183.
[4] Phil. Mag., VI., 1, p. 250, 1901.
[5] Wied. Ann., I., XIII., p. 207, 1897.

produce the fields but the variations produced by the magnetic field are stated only in terms of the current through the magnetizing coils. In 1901 Reicke[1] made an experiment in which he determined current-potential or characteristic curves for discharge in a magnetic field. In his experiment the discharge chamber was placed near one end of a cylindrical magnet and in a diverging field. His record shows the values of the field strength at several points along the discharge path. The longitudinal component of the magnetic field did not exceed 100 C.G.S. units at the electrode farthest removed from the magnet.

Recently there has been a renewed discussion of the effect produced by a longitudinal field both in high vacua and pressures ranging up to one or two millimeters. An article by Strutt[2] reviews some work done by C. S. E. Phillips[3] and extends his experiments along some lines. Both Phillips and Strutt noticed, among other things, that when two cylindrical iron electrodes are in high vacuo a discharge passes for a greatly reduced potential when the iron electrodes are magnetized.

In some cases the discharge potential was reduced from several thousand volts to between 350 and 400, only slightly more than the cathode fall in potential.

J. S. Townsend[4] comments on Strutt's experiment and believes the reduction in potential is due to the increase in path which electrons will have in a magnetic field of this kind. A helical motion will increase the effective path through which they move, thereby increasing the number of collisions which in turn will produce a supply of ions necessary for the maintenance of a current.

F. Horton[5] also comments on Strutt's work as well as on some results recently obtained by himself and in the main agrees with Townsend. He suggests that with strong fields ions may be diverted by the field and a critical field will be obtained when the loss from one effect balances the gain resulting from increases in collision.

The very interesting articles of More and Reiman,[6] More and Mauchley[7] and Righi[8] discuss the possible effects of a magnetic field on the discharge potential.

More and Mauchley maintain that the effect of a longitudinal field is not to produce a new type of ray but that the effect of a longitudinal

[1] Ann. d. Phys., VI., 4, p. 592.
[2] Proc. Roy. Soc., A 89, Aug., 1913, p. 68.
[3] Roy. Soc. Proc., 189, Vol. 64, p. 172.
[4] Phil. Mag., VI., 26, Oct., 1913, p. 730.
[5] Phil. Mag., VI., 26, Nov., 1913, p. 902.
[6] Phil. Mag., Nov., 1912, p. 840.
[7] Phil. Mag., Aug., 1913, p. 252.
[8] Phil. Mag., Nov., 1913, p. 848.

field upon the production of the so-called magnetic rays is to reduce the cathode fall in potential so that a moderate potential will effect a discharge. These possess peculiarities which lead Righi to designate them magnetocathodic rays but More and his colleagues evidently regard them as cathode rays with some features accentuated and these peculiarities are brought out by a delicate adjustment of pressure, potential and a magnetic field but that the latter is not essential.

The article by More and Reiman suggested to the author the desirability of finding out the effect of a magnetic field on a discharge when the conditions were simplified to a greater extent than in some of the previous work. The author has no criticism of previous experiments but wishes to point out that the conditions in many of them were not reduced to the most simple terms. An effort was here made to produce a discharge between plane parallel electrodes having the electric and magnetic field parallel and uniform. The measurements made consisted of the potential required to maintain a steady current whose magnitude was measured while the magnetic field was varied from 0 to 10,000 C.G.S. units. Furthermore, these were obtained under different pressure conditions and for several gases. Fig. 1 indicates the arrangement of the discharge chamber

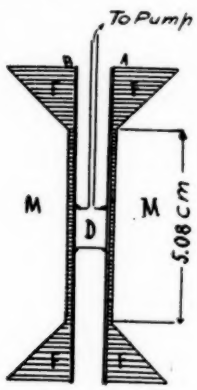

Fig. 1.

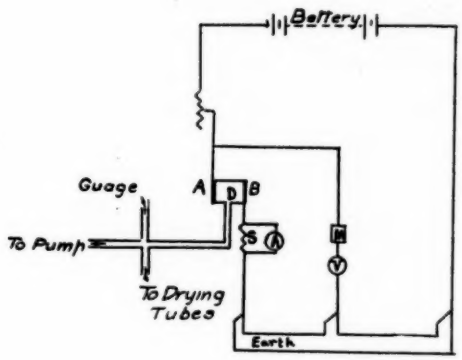

Fig. 2.

in its relation to the two fields. The discharge chamber *D* was a glass tube 14 mm. long and 12 mm. diameter. This was closed at the ends by the electrodes *A* and *B* which were brass plates 8 cm. in diameter. The chamber *D* was placed in the region where the field would be most uniform. The electrodes were backed with fiber 1/32 inch thick and mounted on the faces of the magnet poles *MM* by means of fiber collars *FF*. The tapered pole pieces were 5.08 cm. across the face. An exploring coil showed that the magnetic field in the central region between the

poles was uniform. Fields of 10,000 C.G.S. units were obtainable with this gap.

Fig. 2 indicates the electrical arrangement. One terminal of a battery of 400 storage cells was earthed while the other was connected to the electrode *A* of the discharge chamber through a high variable resistance. The second electrode of the chamber was earthed through a low resistance which formed a shunt, *S*, for a D'Arsonval galvanometer, *A'*. This served to measure the current passing through the discharge chamber. A Weston voltmeter, *V*, with a multiplier, *M*, measured the P.D. between *A* and the earth. The discharge chamber was connected with pump, McLeod gauge and drying apparatus through a small glass tube. Confining the discharge to the central portion of rather large electrodes and in the central portion of the magnetic field approximates rather closely the end desired, viz., to secure uniform and parallel fields. The glass walls enabled changes in the appearance of the discharge to be readily noted.

The motion of the ions under the pressures used, is no doubt a complicated one. In developing the theory of the path which ions follow, it is assumed that saturation is not attained; but in the luminous discharge saturation is attained. It is customary to regard intense ionization as a condition for luminosity. Hence while the magnetic and electrical

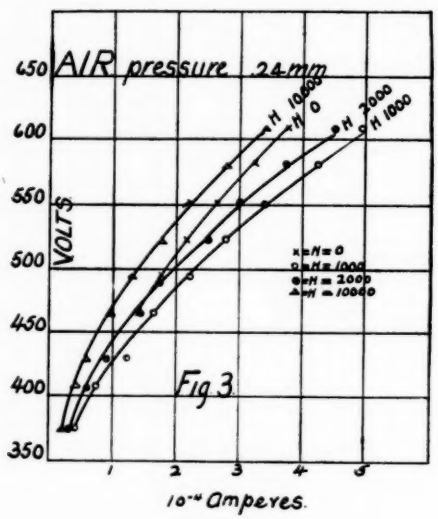

Fig. 3.

fields may be applied in the most simple way the results of collisions will no doubt make the motion of the ions a very complicated one.

Fig. 3 indicates the effect of applying a magnetic field at a pressure

less than the critical pressure. The line designated $H = 0$ gives the current and potential values for zero current in the field coils. The core of the magnet was of very soft iron and the current was reversed

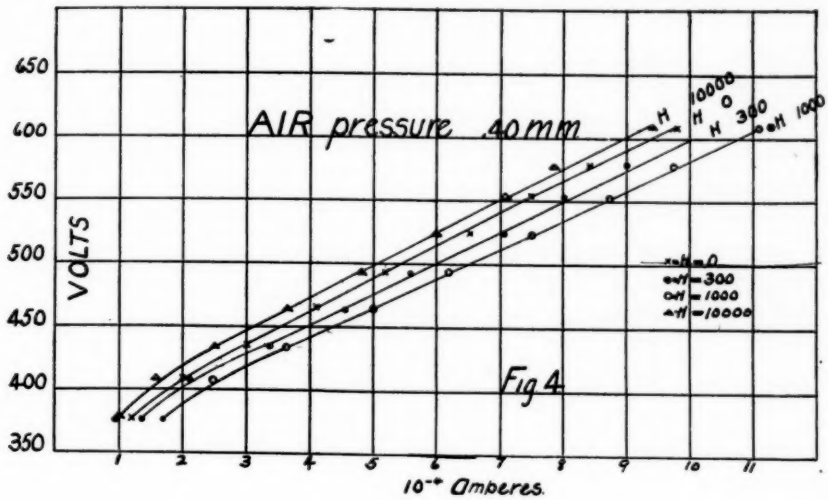

Fig. 4.

with diminishing values until the circuit was broken. However, there is probably some residual magnetism and the field was not strictly zero. It will be noted that with fields up to 1,000 units the discharge current

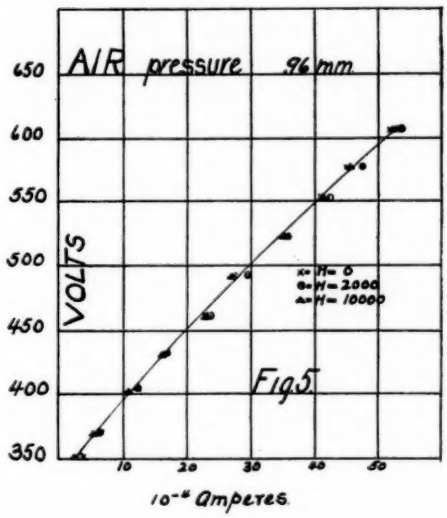

Fig. 5.

for any potential is increased. In fact at this pressure a potential which will not produce a discharge under the action of the electric field alone

will, upon applying a magnetic field, cause the discharge to pass. Reversing the polarity of either electric or magnetic field does not modify the current. I noted, as Almy had previously noted, that when the field was

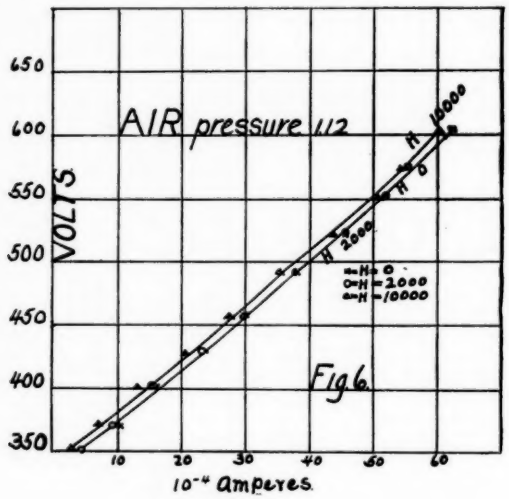

Fig. 6.

applied, the appearance of the discharge changed. Instead of a soft glow filling the tube a series of blue stream-like filaments appeared along

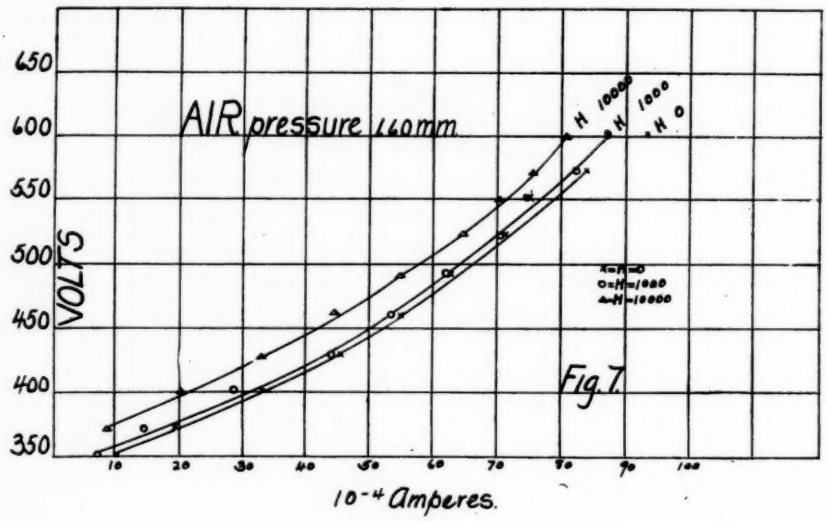

Fig. 7.

the axis of the tube and while the glow did not disappear it was visibly affected by the magnetic field. The current for a given potential increased with field strengths up to 1,400 units; beyond that the current

decreased. In some earlier experiments a less powerful magnet was employed with which fields of only 4,500 units could be obtained. The same effect was noted, viz., that above a critical value of the field the

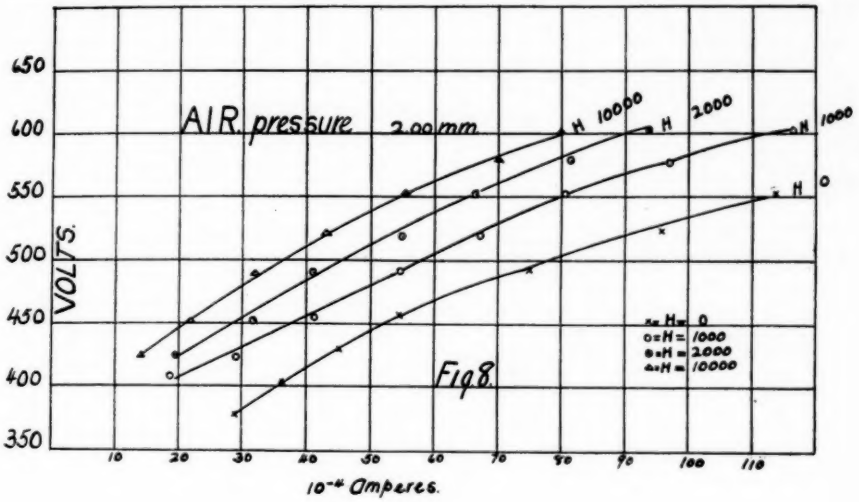

Fig. 8.

current became less with increase in field strength but the field was not sufficiently strong to reduce the current to the value for $H = 0$. With

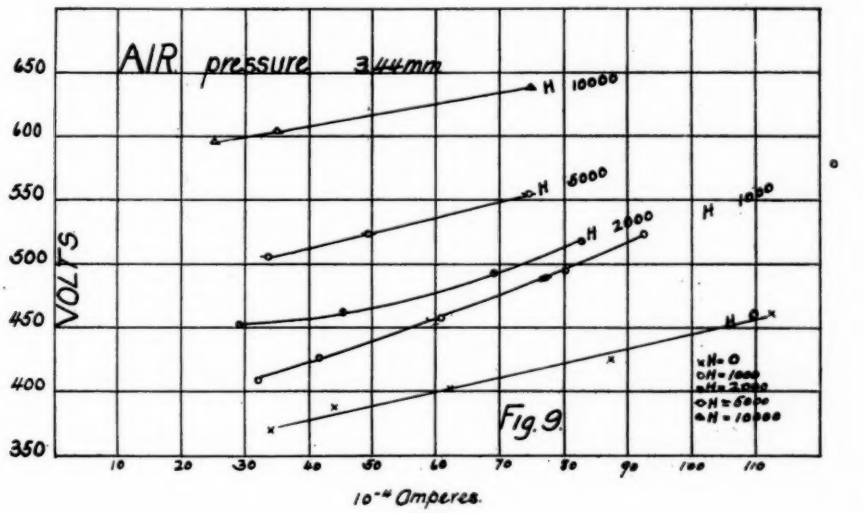

Fig. 9.

the larger magnet using 10,000 C.G.S. units the current value was reduced below the values for zero field.

The figures which follow indicate the influence of pressure change.

It may be noted (Fig. 4) that when the pressure is .40 mm. a field of 1,000 units increases the current, 2,000 units (not shown in figure) pro-

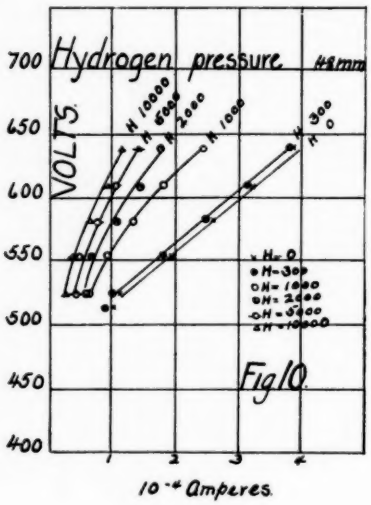

Fig. 10.

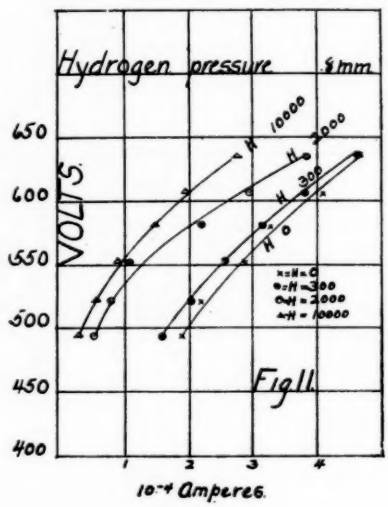

Fig. 11.

duces no further increase but rather a slight diminution. With 10,000 units the current is reduced decidedly below the value for no field. These experiments were performed before some of the recent discussions to

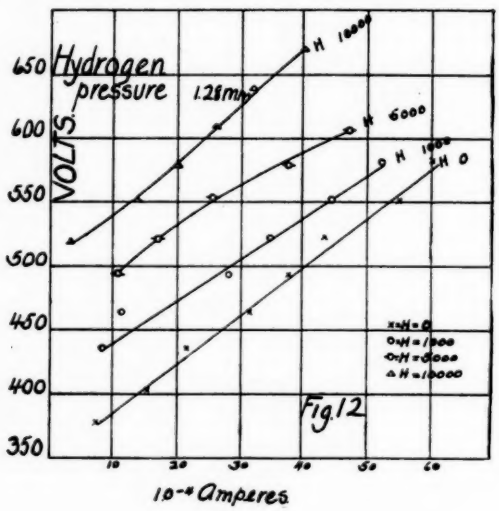

Fig. 12.

which reference has been made occurred, but the trend of the curves indicates that for low pressures increasing the magnetic field would lower the discharge potentials and this would continue until rather strong

fields were produced. It would be necessary, for example, at pressures lower than .24 mm. to obtain a field of strength greater than 1,400 units before further increase in field caused a decrease in current and a very intense field to reduce the current to the value secured when H was 0. From my own experience in this experiment it seems that More and Mauchley are quite correct in stating that at pressures of .1 mm. the effect of the magnetic field is to reduce the effective cathode fall in potential.

At pressures of .96 mm. and 1.12 mm. (Figs. 5 and 6) the effect of the

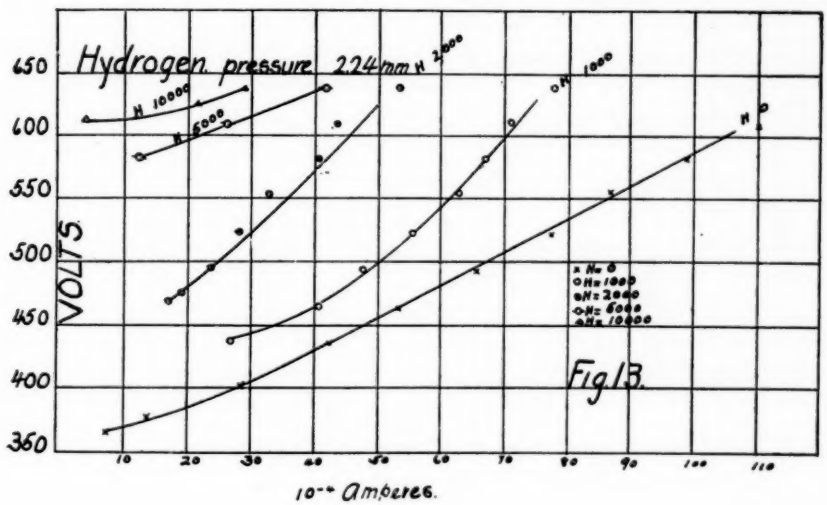

Fig. 13.

magnetic field is very small. A set of measurements made at a pressure of 1.04 mm. show variations of less than one per cent. A curve for this pressure is not shown, however. The readings taken persistently indicate that for the higher potentials the effect of the field is to increase the current slightly while for the lower potentials the current is reduced. These variations are small and would not appear in the graph on the scale chosen. It must be borne in mind that the potentials used were not greatly in excess of the cathode fall in potential and that the potential gradient between the electrodes for a portion of the distance is not the total potential difference divided by the distance separating the electrodes. It may be possible then, that a change in potential from 375 to 400 volts will double the gradient which occurs over a considerable part of the path. This pressure range is very near the critical pressure. Increasing the gas pressure above the critical pressure causes a very large increase in current under normal conditions. Attention is called to the fact that the value of the abscissæ differs in the various figures. It is

quite impossible to plot these on the same scale on account of the large changes in current produced by pressure variation. At pressures above the critical pressures the effect of the field is to greatly reduce the current.

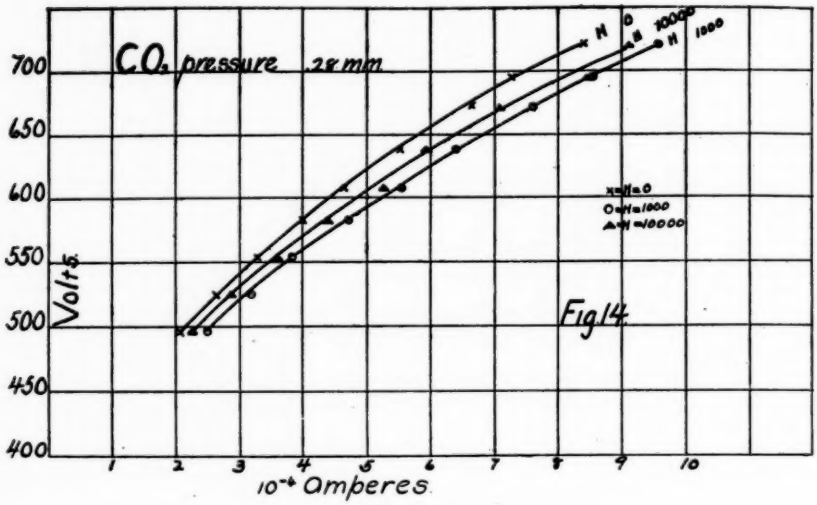

Fig. 14.

In fact at pressures of 3 mm. or more the battery was not sufficient to start the discharge in the presence of a moderate field. It was necessary

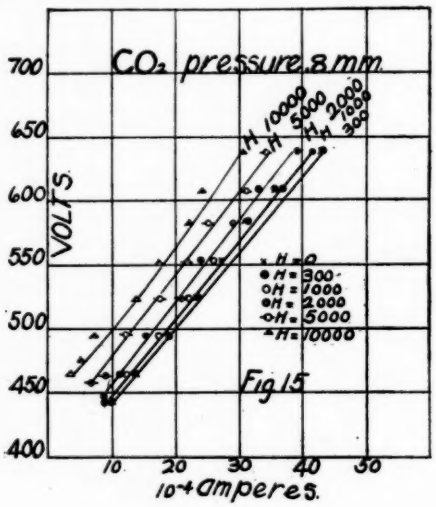

Fig. 15.

to start the discharge, then to apply the field. Unless the potential was maintained at sufficiently high value the discharge would be quenched. This is exactly the reverse of what occurs at the low pressures for in that case a discharge could be started in a magnetic field which could not be maintained when the field was withdrawn.

Figures 10 to 13 show the results of some experiments on hydrogen. The hydrogen prepared in a Kipp apparatus was purified and dried. At the lowest pressure used, a field of 300 gauss reduced the discharge current. A very feeble field, however, would increase it slightly. At higher pressures all fields applied reduced the current. The author is skeptical about the purity of the hydrogen but prepared it in the usual

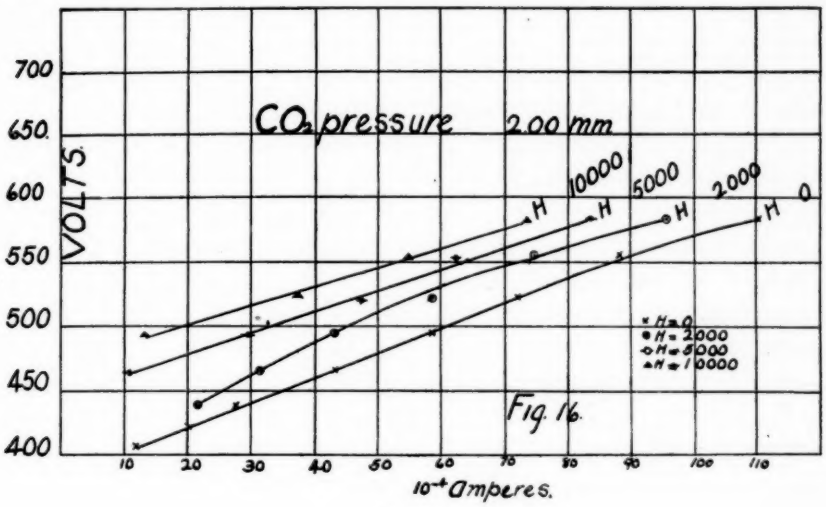

Fig. 16.

manner. Carbon dioxide shows the same general results as air. At the lowest pressure .28 mm. the application of a field of 1,000 units increased the current, 2,000 units increased it still more. With 5,000 units a diminution of current occurred which was not reduced to the value obtained for $H = 0$ with the application of 10,000 units. In few cases are all of the data plotted. Measurements were made with fields of strength 0, 300, 1,000, 2,000, 5,000, 10,000 C.G.S. units. Many intermediate values are omitted in the plotted results. They have served, however, as a satisfactory check upon the other values. In so far as consistent results were obtained they were made possible by operating on a seasoned gas. In order to obtain results which can be repeated and checked several or any number of times it seems necessary to thoroughly dry the gas and to let the discharge pass through it for an hour or more. After such a period of seasoning the gas appears to attain a steady state and the quantitative results can be duplicated with an accuracy of less than one per cent. from day to day. This is not true for a fresh gas.

Before the discussion of Townsend and of Horton appeared the author had entertained much the same view as to the cause of the changes

effected by the magnetic field. For pressures below the critical value the helical motion of the electrons will increase the effective path and ionization by impact will be increased. There is also a force tending to divert the ions from the field if their motion should have a transverse component. With the higher fields the loss due to their diversion would be greater. When the loss due to their diversion becomes greater than the rate of evolution of fresh ions the stronger fields would cause an increasing diminution. For pressures above the critical pressure there is under normal conditions a rapid ionization and the increase due to the helical motion is more than offset by the large number diverted.

The study of a large number of cases leads me to believe there is no critical pressure at which the magnetic field is ineffective at all voltages. For a particular pressure there is a field value that will produce no effect at a certain potential but for potentials slightly above this an increase in current will occur while for lower potentials a reduction of the current is obtained. Some experiments are in progress to test the questions raised. It appears that by increasing the area of the electrode, *i. e.*, using a discharge chamber of larger section, the current density would not be altered by the factor which increases the ionization, *i. e.*, the helical motion of the electrons projected from the cathode, but the factor tending to reduce the current due to the diversion of the ions would be decreased. The discussion of More and Righi on the magnitude of the fields necessary to reduce the cathode fall in potential at low pressures has caused the work so far performed to be published perhaps a little prematurely.

SUMMARY.

1. Quantitative measurements on the effect of a longitudinal magnetic field on a luminous discharge have been made in three gases above and below their critical pressures.

2. Measurements in a uniform magnetic field varying from 0 to 10,000 C.G.S. units have been made.

3. The results indicate that at pressures below the critical pressure a weak field increases the current obtained by a given potential difference while strong fields reduce it. They are shown quantitatively.

4. The lower the gas pressure the greater must be the critical value of the magnetic field to secure a reduction of the current.

5. Pressures close to the critical pressures show small effects due to magnetization but above the critical pressure the longitudinal field reduces the current.

PHYSICAL LABORATORY,
OHIO STATE UNIVERSITY,
COLUMBUS, OHIO, November 24, 1913.

ANOMALOUS TEMPERATURE EFFECTS UPON MAGNETIZED STEEL.

By N. H. Williams.

A SOMEWHAT striking case of anomalous magnetization was described about a year ago by Smith and Guild.[1] Steel rods 7 cm. long were magnetized and then heated. In all cases in which the carbon content was greater than .15 per cent. the magnetism was reversed in the neighborhood of 200° C. The effect was most marked when the percentage of carbon was .85 of one per cent. In that case the negative intensity at 210° was about 10 per cent. of the maximum residual intensity before heating. With further rise of temperature, this negative flux very gradually decreased and finally disappeared at about 700° C.

If, after the temperature had been raised to 210° and a negative magnetic moment established, the specimen were allowed to cool, it partially regained its former positive magnetism.

The explanation of the phenomenon by the authors can be gathered from the following quotation from their paper: "The facts, therefore, suggest the following view of the course of events within each rod. Withdrawal of the magnetizing field leaves the rod subject to the influence of its own self-demagnetizing force, which at first is considerable. This force, acting upon the iron and upon the carbide tends to reverse the polarity of both. The alignment of the iron is more easily disturbed than that of the carbide and a greater amount of reversal is produced in the former. The reversing field diminishes continuously, and when it becomes incapable of producing further change, the feeble residual polarity is made up of a small positive polarity due to the carbide and of a still smaller negative polarity due to the iron.

"When the rod is heated, the polarity of the carbide diminishes more rapidly than the opposite polarity of the iron for several reasons. One of the most important is that the carbide is approaching its transition temperature more rapidly than the iron, and another is that, until the zero moment in the neighborhood of 200° is passed, the demagnetizing field tends to maintain the negatively magnetized constituent."

If this explanation be accepted, we must imagine an intimate mixture

[1] Proceedings of the Physical Society of London, August 15, 1912.

of two different kinds of particles in which the magnetic induction is in one sense in one constituent of the mixture and in the opposite sense in the other; moreover, the reversal of the polarity of one constituent was accomplished by the action of the other.

So long as we think of the substance composing the magnet as a continuous homogeneous medium of definite permeability, it is perfectly correct to say that at an interior point the only field acting is the demagnetizing field due to the ends but when we conceive of the magnet as made up of discrete particles of two kinds of substance in intimate mixture we are no longer entitled to treat the substance of the magnet as a homogeneous, continuous medium. The field brought to bear upon a molecular magnet within the iron would be the field existing in the intermolecular space, which is by no means a demagnetizing field.

Hopkinson's experiments show a large increase of susceptibility of iron and steel to *small* magnetic fields when the temperature is raised. This would lead us to expect considerable self-demagnetization with rise of temperature, but it would not account for the reversal.

The work described in the present paper was undertaken in the hope of furnishing further data upon which to base an explanation of this curious phenomenon.

A solid bar of steel 7 cm. long and having a cross-sectional area of 1.75 sq. cm. was used. The steel contained .85 of one per cent. of carbon. The bar was magnetized by placing it within a helix of many turns of wire, the current being supplied from a storage battery. After the bar was magnetized it was fastened within a frame upon which a test coil was arranged to slide so that it could be brought quickly to a position where it surrounded the magnet. The test coil was connected to a ballistic galvanometer and the frame and coil were immersed in an oil bath. It was assumed that the throw of the galvanometer when the coil was thrown over the magnet or when it was suddenly taken off would be proportional to the residual flux in the metal. The conclusions drawn from the work are not affected if this assumption is considered as only approximately correct. The oil was heated by Bunsen burners and the temperature was measured by a mercury thermometer. In this way the residual flux was measured at brief intervals as the temperature increased from 20° to 220°.

The experiments upon this specimen showed the reversal of polarity that was expected but the magnitude of the reversed flux was not as large in comparison with the maximum residual flux as was obtained by Smith and Guild. Fig. 1 shows the results. Temperatures are plotted as abscissæ and galvanometer deflections (proportional to magnetic

flux) as ordinates. The reversed deflection at 195° was about 5 per cent. of that due to the maximum residual flux and upon cooling, the specimen recovered about a quarter of its original positive magnetism. However, the experiment may be so arranged as to avoid the appearance of this

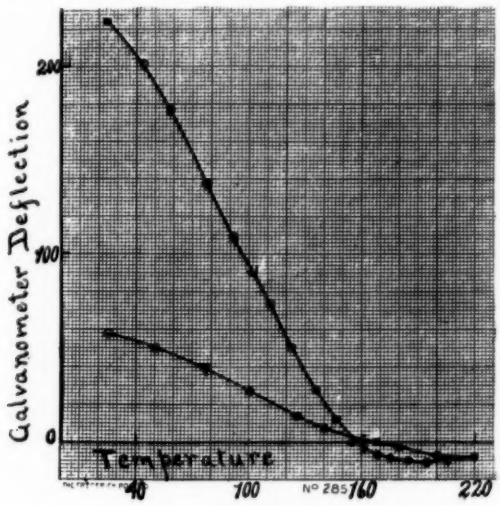

Fig. 1.

anomalous behavior. Fig. 2 shows results obtained under the same conditions as those pertaining to Fig. 1 with this exception: This time after magnetizing the steel it was removed from the coil without opening the magnetizing circuit, whereas in the former case the circuit was broken at the switch before the iron was removed from the helix.

It will be observed that in Fig. 2 the flux starts at a very much higher value and diminishes as the temperature rises, coming to zero at about 190°, but that it does not reverse. If the end effects were responsible for the reversal there should have been a larger reversed magnetization in the second case than in the first, since the residual flux which produced the end effect was twice as large in the second case as in the first. Since, however, there was none at all we seem justified in the conclusion that end effects are not the cause of the reversal but that the explanation is to be found in the oscillatory spark at the switch when the circuit is opened. The condition that the discharge shall be oscillatory in a given system is expressed by the relation $R^2/4L^2 < 1/LC$, R being resistance, L inductance and C capacity.

The circuit, here considered, consisted of a storage battery, a coil of wire and a knife switch. The capacity is therefore extremely small and we may be certain that the above condition is fulfilled and that an

oscillatory current will flow through the coil when the switch is opened. The period of this oscillation is

$$T = \frac{2\pi}{\sqrt{\frac{1}{LC} - \frac{R^2}{4L^2}}}$$

or approximately $2\pi\sqrt{LC}$. Since C is extremely small the period is also extremely small.

The effect of such a current on the magnetism of the steel core would

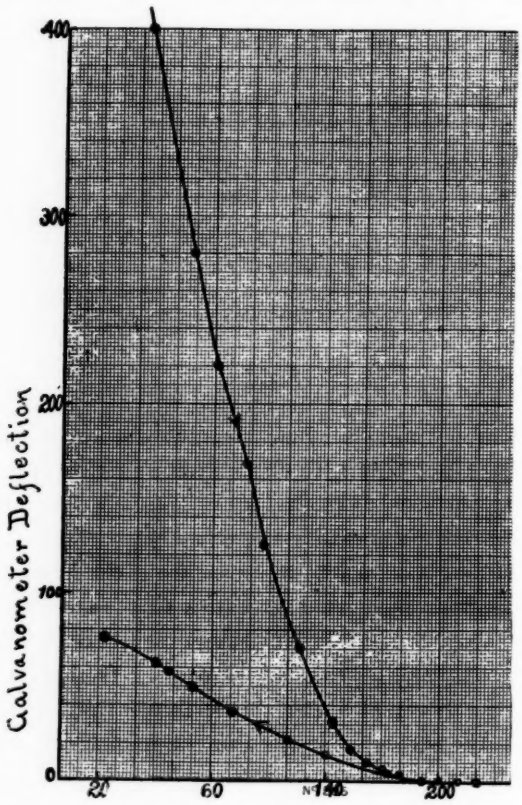

Fig. 2.

be confined to a thin surface layer, the eddy currents in the outside layers being sufficient to protect the inner portion of the core from its action. The first reversed current of this oscillatory discharge would be larger than any subsequent current in either direction and the magnetic effect of this current in conjunction with the demagnetizing field due to the ends might produce a reversal of the outside layers of the core.

It is almost inevitable that steel with such high percentage of carbon

should be slightly harder in its outside layers than at the interior of the specimen. We should then expect that with rise of temperature the magnetism of the outer layers would persist after that of the softer interior had disappeared and hence that the resultant magnetic moment would be reversed at the high temperature.

The authors previously mentioned also studied the effect of a rise of temperature upon a specimen that had been first magnetized strongly and then subjected to a demagnetizing field just strong enough to leave the specimen apparently demagnetized. They stated that under these conditions the negative magnetism that developed with rise of temperature was much stronger than in the other cases and that it occurred after a very slight rise of positive magnetism. The author has been unable to reproduce these results. What has happened in each case is a rise of positive magnetism, *i. e.*, a flux in the direction of the original strong magnetizing field and whether the flux finally reverses at 190° is again determined by the method of magnetizing and demagnetizing the specimen.

Fig. 3 shows the results when the specimen was first highly magnetized

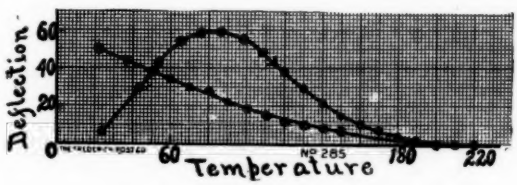

Fig. 3.

then demagnetized; in both cases the steel being removed from the coil before the switch was opened thus avoiding entirely the effects of oscillatory currents. With rise of temperature the positive magnetism develops, reaches a maximum at about 80°, then decreases reaching zero at about 200°. On cooling, the steel recovers over 80 per cent. of its maximum flux. There is no indication of a reversal.

Two other cases naturally suggest themselves: (*a*) The specimen might be magnetized and the circuit broken at the switch, then demagnetized without breaking the circuit. We should expect then a reversal of magnetism at high temperatures. (*b*) The specimen might be magnetized and removed from the coil without breaking the circuit, then subjected to a demagnetizing field, the circuit being opened at the switch in the latter operation. The effect of the oscillating current would be to reverse the outer layer with respect to the final field, *i. e.*, to magnetize it in the direction of the original field, which we have called positive. So

in this case we should not expect a reversal of magnetism with rise of temperature nor indeed should we expect to be able to reduce the flux to zero in the neighborhood of 200°.

Figs. 4 and 5 represent data obtained under the conditions described

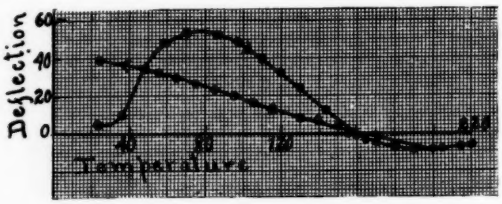

Fig. 4.

under (*a*) and (*b*) respectively, and they are in accordance with the statements there made as to what should be expected.

A good illustration of the effect of the oscillatory current was found while obtaining data similar to those of the last two curves. The specimen was magnetized strongly in the positive direction and then subjected to a negative field such that if the bar were slowly withdrawn from the field, it retained negative polarity sufficient to produce a throw of the galvanometer equal to − 102. This same negative field was again applied and the current interrupted at the switch, thus giving rise to

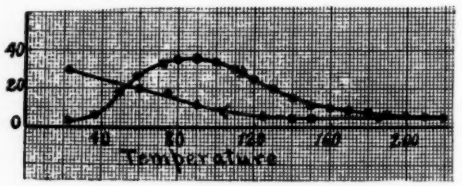

Fig. 5.

oscillations. The residual magnetism was then found to be positive and sufficient to produce a deflection + 60. Again the field was applied without permitting oscillations and the residual flux produced a deflection of − 106. Another application of the same field followed by a break at the switch caused positive residual magnetism, and so on indefinitely.

If the explanation proposed for this apparent anomaly be correct, the phenomena may be classified with other cases which have been described in detail in a recent paper by B. O. Peirce, on "The Anomalous Magnetization of Iron and Steel."[1]

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[1] Proceedings of the American Academy of Arts and Sciences, March, 1912.

CALCULATION OF A DAMPING RECTANGLE TO PRODUCE CRITICAL DAMPING IN A MOVING COIL GALVANOMETER.

BY PAUL E. KLOPSTEG.

IF a moving coil galvanometer is used ballistically, it is ordinarily desirable to have the coefficient of damping small, principally because much damping reduces the throw produced by a given quantity of electricity; there are, however, certain conditions under which it is expedient to have the instrument critically damped. When the galvanometer is to be used for steady deflection work it is often not only expedient but imperative to have the motion just aperiodic. The advantages of critical damping have been discussed by O. M. Stewart[1] and Jaeger.[2]

The usual procedure in changing from a ballistic to a deflection galvanometer is to increase the damping to aperiodicity by attaching to the coil a closed wire rectangle, usually of the same mean area as the coil. However, since a certain coil may be used with different kinds and lengths of suspension fibers and, furthermore, since there is considerable initial damping when the galvanometer is used on a closed circuit of high resistance, the damping rectangle usually furnished by the manufacturers may or may not make the coil just aperiodic. In most cases the boundary condition between periodic and aperiodic motion is not realized. A method is given in this paper by means of which the proper diameter of a wire for a damping rectangle may be found in order that, for given conditions, the galvanometer may be critically damped.

We shall assume at the outset that the magnetic field in which the coil is suspended is uniform, *i. e.*, that the damping rectangle which is to be attached to the face of the coil will swing in a field of the same strength as does the "mean" turn of the coil. In a previous paper[3] the author

[1] PHYS. REV., 16, O.S., 1903, p. 158.

[2] Ztschr. f. Instrumentenk., 23, 1903, pp. 261 and 353.

[3] Klopsteg, PHYS. REV., 2, N.S., 1913, p. 390. After the publication of the paper here cited, and after the present paper had been submitted for publication, my attention was called by Dr. I. Fröhlich of Budapest to his paper, which I had overlooked, appearing in "A Mathematikai és Természettudományi Értesítö", Vol. VII, 1889, p. 44, under the title, "Zárt elektromos vezetök lengése homogén mágnesi térben", dealing with the vibrations of a closed conductor in a homogeneous magnetic field. Dr. Fröhlich develops an equation

developed an equation for field intensity, based upon critical damping, of the form

$$H = \frac{2\sqrt{10^9 I_0}}{nld}\sqrt{\frac{R_0}{T_0}(\pi - \lambda)}, \tag{1}$$

in which I_0, n and ld are, respectively, the moment of inertia, number of turns and mean area of the coil, T_0 is its period and λ its logarithmic decrement on open circuit, while R_0 is the total resistance in ohms of the circuit containing the galvanometer. The resistance R_0 is such that damping is critical. If in this equation we place $n = 1$ and solve for R_0, the result will be the resistance of a single closed turn of wire such that the induced current in it due to the cutting of the field may be of proper magnitude to bring about the desired effect. The equation becomes

$$R_0 = \frac{(Hld)^2 T_0}{4 \times 10^9 I_0(\pi - \lambda)}. \tag{2}$$

The damping rectangle having the same mean area as the coil, the total length of wire will be $2(l + d)$; the diameter of the wire is then, in centimeters,

$$D = \sqrt{\frac{8\rho(l + d)}{\pi R_0}}, \tag{3}$$

ρ being the specific resistance of the metal from which the wire is drawn. Combining (2) and (3),

$$D = \frac{1}{Hld}\sqrt{\frac{3.2 \times 10^{10}\rho I_0(l + d)(\pi - \lambda)}{\pi T_0}}. \tag{4}$$

In galvanometer fields of the type represented in Fig. 1, with the usual

Fig. 1.

which gives the relationship between the intensity of the field and quantities to be obtained by measurement or calculation from the closed conductor. Briefly, his method is based upon the difference in the periods of the closed conductor when vibrating in zero field and in the field under investigation, whereas my formula makes use of the difference in the logarithmic decrements when the coil vibrates on open and closed circuits, respectively. In my paper (p. 392, eq. (10)) it was shown that the difference in periods corresponding to any two logarithmic decrements is very small, which fact alone would make the method of Dr. Fröhlich impracticable; on the other hand, the comparatively large differences in the logarithmic decrement are readily measurable with great accuracy. Another objection to using a closed conductor is the inflexibility of the method, on account of the fixed resistance of that conductor. For the best results by such a method, the damping must be great enough to make an appreciable difference in the period, but not so great as to make the vibrations die out rapidly. This means, in its practical application, that any one closed conductor could be used over a very limited range only; whereas, in the description of the damped coil method, it was shown that it is entirely practicable to use the same coil for measurements of a few gausses up to several thousand. Dr. Fröhlich gives no experimental data. Had he tried his method he would have been at once confronted by the above mentioned limitations.

type of coil used in such fields, the vertical wires of the rectangle are approximately in the position shown by the dots in the figure when the coil is undeflected. The damped coil method[1] of determining H for equation (4) gives as its value the field intensity at the position of the "mean" turn of the coil at rest. Evidently the value so obtained is higher than the field strength at the position of the rectangle, consequently equation (4) will give a value of D which is too small. To correct for this difference, the field was measured in several galvanometers of this type both at the null position of the coil and at the position of the rectangle. The ratio between these two values was found[2] to be 1.30. Usually the damping rectangle is made of copper wire; in this case $\rho = 1.69 \times 10^{-6}$ (15° C.); introducing this value and the ratio 1.30 into equation (4) it becomes

$$D = \frac{170}{Hld}\sqrt{\frac{I_0}{T_0}(l+d)(\pi - \lambda)}. \qquad (5)$$

To apply formula (5), H is determined by the method mentioned above, l and d are readily found by means of a stage microscope, while λ and T_0 are obtained in the usual manner. It should be observed that λ is not necessarily the logarithmic decrement on *open* circuit; when, for example, the galvanometer is used on a closed circuit of such resistance that damping is not critical, λ is the logarithmic decrement for this special condition. I_0 is found by the method of comparing the periods of the coil and of a disk of known moment of inertia, each in turn suspended from the same fiber. The value of D having been calculated, the wire gauge corresponding most nearly with this value is selected for the rectangle.

The addition of the mass of the rectangle to that of the coil has the effect of increasing to some extent the values of both I_0 and T_0. It is unnecessary to make a second approximation because of the fact that the value of the fraction I_0/T_0 is changed only slightly and that this fraction is under the radical sign, the percentage change being thereby halved. Practically, one is also limited to the standard wire gauges, which admits of some latitude in the value of D. To determine the effect of the added mass of the rectangle, an experiment was tried, using an

[1] Loc. cit.

[2] For any particular type of field or depth of coil (distance from face to back) the ratio between field strengths may be determined by the damped coil method, the equation for the ratio being

$$\frac{H}{H'} = \sqrt{\frac{T_0'}{T_0}\frac{\Lambda - \lambda}{\Lambda' - \lambda'}}$$

when the same value of R is used in both cases. The value 1.30 is understood to refer to the case only which is discussed above.

"open" rectangle of the wire gauge given by one calculation, and redetermining the quantities appearing in the equation. There was a slight change in the new value of D, but not sufficient to necessitate using a different wire gauge. The size found by the first calculation produced damping as nearly critical as could be judged.

When the number of turns in the galvanometer coil is known, a formula more simple in its application—one which involves the determination of neither H nor I_0—may be found by making use of the equation[1]

$$H = \frac{2\sqrt{10^9 I_0}}{nld} \sqrt{\frac{R}{T_0}(\Lambda - \lambda_0)}, \tag{6}$$

where Λ is the logarithmic decrement corresponding to a total resistance R in the circuit which is not sufficiently small to make damping critical, and λ_0 is the logarithmic decrement on open circuit. The other quantities are defined as before. From this equation and (2) we find

$$R_0 = \frac{R}{n^2} \frac{\Lambda - \lambda_0}{\pi - \lambda}, \tag{7}$$

which equation, when combined with (3) gives

$$D = \sqrt{\frac{8\rho n^2 (l + d)(\pi - \lambda_0)}{\pi R(\Lambda - \lambda_0)}}. \tag{8}$$

Introducing the constant 1.30, explained in connection with (5), and substituting for ρ the value before given, we find that for a copper wire damper

$$D = 0.00269n \sqrt{\frac{(l + d)(\pi - \lambda)}{R(\Lambda - \lambda_0)}}. \tag{9}$$

Evidently, when the galvanometer is used in open circuit work, λ_0 and λ of equations (8) and (9) are equal; when the coil is on closed circuit, λ is, as before, the logarithmic decrement for this condition, while λ_0 remains the logarithmic decrement on open circuit.

The results obtained by equations (5) and (9) were found in good agreement in all cases tried, which included several types of moving coil galvanometers and three kinds of upper suspensions, viz.: 3-mil and 1.5-mil phosphor bronze strip and 1.5-mil phosphor bronze wire.

SUMMARY.

In brief, this paper gives the development of two equations for finding the proper size of wire to be used in damping rectangles in order that critical damping may be obtained in moving coil galvanometers. The

[1] Loc. cit.

first equation is used when the number of turns in the coil cannot be ascertained, the second when this number is known.

The suggestion is made, in conclusion, that manufacturers be requested to furnish with their galvanometer coils the values of n, l, d and I_0. Such data would minimize the number of quantities to be determined by the experimenter in measuring fields by the damped coil method, and would greatly simplify the obtaining of data for calculations such as are mentioned in this paper.

Physical Laboratory,
The University of Minnesota,
December, 1913.

CHANGE OF PHASE UNDER PRESSURE.

I. THE PHASE DIAGRAM OF ELEVEN SUBSTANCES WITH ESPECIAL REFERENCE TO THE MELTING CURVE.

BY P. W. BRIDGMAN.

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Apparatus and experimental method 130
Details of experiment and computations.
Discussion.
Summary.

INTRODUCTION.

THIS paper is the first of a projected series of papers dealing with the various problems offered by the phenomena of change of phase under pressure. At high pressures we are concerned with phase changes of only two types, from the fluid to the solid (or crystalline) phase, and from one solid phase to another, since at high pressures the gaseous phase no longer has an independent existence. It is the first of these changes, that from the liquid to the solid, that is to be the special subject of this paper. The problem presented by the change from liquid to solid involves for its complete solution a description of the molecular arrangement of the liquid and the crystal and of the nature of the forces that produce crystallization. Hitherto one narrow aspect of this problem has received almost exclusive attention, the question as to the general shape of the melting curve. Evidently an answer to this question would go far in pointing the way to the essential difference between a liquid and a crystal. Two answers to this question have been regarded as most probably correct; the first is that the liquid-solid curve ends in a critical point, and the second, directly opposed to the first, is that the melting curve passes through a maximum temperature, so that if pressure is raised sufficiently high at constant temperature we may first freeze the liquid to the solid and then melt it again to the liquid. The more particular object of this paper is to settle definitely, with the help of new data, this long discussed question as to the shape of the melting curve.

The data hitherto available have covered a pressure range of about 3,000 kgm. These data are mainly due to Tammann, who measured

the relation between pressure and melting temperature over this pressure range, and also measured for some of his substances, with considerably less accuracy, the difference of volume between solid and liquid along the melting curve. The data presented here cover a pressure range up to 12,000–13,000 kgm. per sq. cm., and a temperature range from 0° to 200°. Over this entire range the relation between melting temperature and pressure has been measured, and the difference of volume between solid and liquid has also been determined. These two kinds of data are necessary and sufficient from a thermodynamic point of view to settle the point at issue. Eleven substances have been experimented on, including simple and complicated organic compounds and three elements. These all indicate the same answer to the question in hand.

For the immediate purposes of this first paper those substances were selected which had only one known modification of the solid, in order not to complicate the study by the entrance of a second solid phase. But four of the substances studied have been found to have new solid modifications at high pressures. It may be, therefore, that polymorphism at high pressures is a common instead of an exceptional phenomenon. The data given in this paper include data that will be used later in the discussion of the relation between different solid modifications. And similarly, some of the data to be presented in future papers may be expected to have a bearing on the narrower question to be discussed here.

SUMMARY OF PREVIOUS WORK AND PRESENT STATE OF THE PROBLEM.

It is proposed to quote here only those papers bearing on the question at issue, the true character of the melting curve. This will omit a few papers giving measurements only, and also much of the earlier work, which was occupied with experimental proof of the validity of the formulas deduced by thermodynamics, at a time when complete confidence apparently was not felt in thermodynamic arguments. Most of the early speculators on the true nature of the melting curve seem to have been guided mostly by analogy with the then recently established critical point between liquid and vapor, and assumed the existence of a similar critical point between liquid and solid. Poynting[1] was one of the earliest of these. He predicted by analogy between water and its vapor that there were two critical points between water and ice; one at − 120° and 16,000 atmos., the other at + 14° and some high negative pressure. Practically no experimental evidence was given. Planck[2] thought that there was a critical point, and deduced some thermodynamic relations which must hold if such a point exists. Peddie[3] also gave thermodynamic relations for a critical point if it exists, and quoted observations

of Bunsen on paraffine suggesting the possible existence of such a point. Amagat[4] then contributed some actual observations up to 1,100 atmos. on the solidification of CCl_4, and stated that the appearance was as if a second liquefaction took place at a higher pressure than that required to produce solidification. In his opinion a critical point seemed likely. Two papers by Damien[5] with new experimental data gave the subject new impetus from the experimental side. His results reached to 200 atmos. and he claimed to have found for several organic substances, not a critical point, but a maximum melting temperature. At temperatures below the maximum the continually increasing application of pressure first freezes the body to a solid and then melts it again. This seems to have been the first suggestion in the literature of such a phenomenon. Barus[6] in 1892 published investigations up to 2,000 atmos. on a number of organic liquids, but his results did not become known until later. He found no evidence of a maximum up to 2,000 atmos., but there was a certain cyclic character in the transformation solid-liquid which reminded him of the unstable part of the isotherms of James Thomson. He seems to have been of the opinion that at high enough pressures there is a critical point. Amagat[7] then published data on water, obtained with the same apparatus as for CCl_4, up to 1,000 atmos. He was of the opinion, although his results do not suggest it particularly strongly, that at high enough pressures there might be an inversion point beyond which ice is more dense than water, so that at high pressures the melting point of ice would be raised by pressure instead of lowered; that is, a minimum point, the reverse of Damien's maximum. Demerliac[8] in two papers next subjected Damien's results to further experimental scrutiny up to 300 kgm. Demerliac's results are usually quoted as supporting Damien's theory, but only because of a misunderstanding. Demerliac found that for the lower pressures of his range his results could be very accurately represented by a formula which predicts a maximum, but that at the higher pressures the results no longer fitted the formula, the temperature tending to approach more and more closely to a limiting value. Demerliac's opinion, therefore, was that the melting curve tends to approach a horizontal asymptote. He nearly reached the asymptote for several substances. The years 1898–99 marked great activity in this field, several of the results appearing without knowledge of the others. Heydweiller[9] published results showing that there could not by any possibility be a maximum at pressures as low as Damien supposed, and was of the opinion that there must be a critical point at high enough pressures. He chose substances to investigate that might be expected to be near their critical points, but he could find no critical phenomena up to pres-

sures estimated to be between 1,000 and 3,000 atmos. At the same time he observed effects of another kind on menthol which he thought were indicative of a critical point. Mack[10] published results up to 2,100 atmos. on several organic substances, and could find evidence of neither a critical point nor of a maximum. His melting curves were nearly linear. Hulett[11]), inspired by Ostwald who was of the opinion that there was a critical point, investigated liquid crystals up to 300 kgm. It seemed natural to suppose that liquid crystals might be near the critical point, but he found on the contrary that the difference between liquid crystal and the liquid became more strongly accentuated at increasing pressure. If there were a critical point, it could exist only at negative pressures. About this time Tammann[12] began to publish his experiments and theory, and he has since then almost monopolized the field. His results cover a range of 3,000 kgm., higher than had been reached hitherto. One of his first services was to explain the remarkable discrepancies between previous experimental results by calling attention to the effect of dissolved impurities. Damien provides a particularly striking example of this; his medium of compression was air, which is dissolved more and more at high pressures. The cycles found by Barus are also similarly explained by the action of impurities. Tammann's theory is well known, and will be described again only briefly. It is, in part, that all substances show a maximum melting point, but this maximum is very much higher than supposed by Damien. Tammann himself was never able to reach it, but supposed that it might be in the neighborhood of 10,000 kgm. for a number of substances. In support of this theory, Tammann shows that we must consider all the thermodynamic elements of the phenomena of melting, the change of volume and the latent heat, as well as the melting curve itself. His data show that the change of volume decreases along the melting curve, while the latent heat increases or remains nearly constant. Now at a critical point the change of volume and the latent heat must vanish together, but at a maximum the change of volume vanishes, while the latent heat remains finite. The data are unquestionably more favorable to the second than to the first of these alternatives, and this constitutes the evidence for a maximum. Still the evidence, even from Tammann's own data, is by no means conclusive, and there have been at least two upholders since then of the idea of a critical point. Weimarn[13] in 1910 argued from the behavior of colloids to the probable existence of a critical point. His argument is briefly as follows. At any pressure, no matter how high, the temperature may be raised so high that the dispersive forces due to the intense molecular agitation overcomes the orienting

forces, so that the substance can exist only in the form of very finely disperse crystals. When the crystals become molecular in dimensions we have achieved continuous passage between the two states, or have reached the critical point. Van Laar[14] also, from an entirely different point of view, has deduced a theory demanding a critical point. This has been described in greater detail elsewhere; briefly, the difference between a liquid and a solid consists in an association of the molecules in the solid, which produces a second loop in the isotherm of James Thomson, with the possibility of a critical point. For substances which contract on freezing, this theory demands that there shall always be a critical point solid-liquid, but never a maximum. Because of an error in one of the figures of the original article, the author stated in a previous summary of van Laar's theory that under some conditions a maximum might occur. In 1911 the author published two experimental papers bearing on this subject,[15] over a pressure range considerably higher than previously reached. The evidence of the first paper, on mercury to 12,000 kgm., was against the existence of Tammann's maximum, but left open the question of a critical point. The second paper, on water to 20,000 kgm., did not give so valuable evidence because of the many abnormalities of water. However, all the evidence suggests that these abnormalities disappear at high pressures. If water can be regarded as really normal at high pressures, then the evidence of water is that there is neither critical point nor maximum, but that the melting curve continues rising indefinitely. Van Laar[16] has since this published a short paper in which he regards the evidence of the mercury as on the whole favorable to his theory, but apparently regards water as too abnormal to make its evidence of much value.

APPARATUS AND EXPERIMENTAL METHOD.

Apparatus.—The apparatus is in essentials the same as that used in previous work[15] and needs only brief description. Some slight changes have been necessitated by the higher temperature reached here, 200° instead of 80°. The apparatus finally used consists of an upper and a lower cylinder, connected by a heavy piece of tubing. The upper cylinder contains the moving piston, actuated by a hydraulic press, by which pressure is produced. The motion of the piston, measured with a micrometer, may be combined with the cross section to give the change of volume of the substance under investigation in the lower cylinder. The upper cylinder also contains the coil of manganin wire, from the change in the resistance of which the pressure is determined. The upper cylinder contains one feature not found in the previously used apparatus. The

compressibility of some of the substances was so high that a single stroke of the piston would not have given the maximum pressure desired. The difficulty was avoided by starting the experiment with initial pressure. To accomplish this, a very minute by-pass was provided at the upper end of the cylinder connecting the interior of the cylinder with an auxiliary pressure pump. The by-pass connects with the interior of the cylinder only when the piston is withdrawn to the extreme position. In this position, pressure was raised to the desired amount, 2,000 or 3,000 kgm., by the auxiliary pump acting through the by-pass, and then the auxiliary pump cut off by advancing the piston slightly beyond the by-pass. It is necessary that the by-pass be very small indeed, otherwise the rubber packing on the moving piston gets blown into it as the piston moves by. A sufficiently minute hole was made by drilling and tapping a hole through the side of the cylinder, and then screwing into the hole a tightly fitting screw, across the threads of which a lateral scratch had been made. The upper cylinder, together with the lower part of the hydraulic press, was placed in a thermostat maintained at about 35°. In this way all temperature corrections of the manganin coil were avoided. A temperature as high as 35° was necessary because the conduction of heat along the connecting tube from the lower cylinder sufficed (when the lower cylinder was as high as 200°) to keep the upper thermostat at nearly 35°.

The lower cylinder contained the substance to be investigated. It was held suspended in another thermostat by the connecting tube, led through a water-tight stuffing box in the bottom of the upper thermostat. The temperature of the lower thermostat was systematically run to 200°. For the higher temperatures, "Crisco," a substitute for lard by the Proctor and Gamble Co., was chosen for the bath liquid, because of its comparative freedom from odor. The temperature regulation was by means of an ordinary mercury contact device. This worked well for the few hours occupied by a single run, but at the higher temperatures trouble might arise if longer runs were necessary, because of a slow drift of temperature due to the very gradual distillation of mercury from the temperature regulator. The difficulty can be largely avoided by carefully designing the mercury bulb. The substance to be investigated, if it was such as not to be attacked by the kerosene which transmitted the pressure, was placed in an open cup, or if it were attacked by the kerosene, it was placed in a steel bulb with a mercury seal, of exactly the same design as was used in investigating the thermal properties of twelve liquids.[17]

The dimensions of the various parts of the apparatus were as follows. The upper cylinder: length 8 inches, outside diameter 4½ inches, inside

diameter 17/32 of an inch, length of stroke of piston 3½ inches. The connecting pipe: length 16½ inches, outside diameter 1½ inches, inside diameter 1/16 of an inch. The connections at the end of this tube were especially heavy, the minimum outside diameter at places where the pressure was entirely internal was ¾ of an inch. The lower cylinder had the dimensions: length 10½ inches, outside diameter 4½ inches, inside diameter 11/16 of an inch, depth of interior cavity 9 inches. All parts of the apparatus were made of the Halcomb Steel Co.'s electric furnace chrome-vanadium steel, which has proved itself the best yet found for the purpose.

The apparatus in the form just described was not the form first used. In the first form there were three pressure cylinders and two connecting pipes. In the one cylinder the pressure was produced by the moving piston, in the second was placed the manganin coil with which pressure was measured, and in the third was the liquid under investigation. There was only one thermostat, around the third cylinder. Conduction of heat to the second cylinder was avoided by a water jacket with running water around the connecting tube. The temperature fluctuations in the second cylinder were not large and could be readily corrected for. The fatal weakness in this original apparatus was in the connecting pipes. The connections were of a type in which the end of the tube was turned down to 5/16 of an inch and threaded with a 32 thread, bringing the minimum outside diameter of points where there is only internal pressure to about ¼ of an inch (the inside diameter was 1/16 of an inch). The result was that the tubes were invariably torn apart at the connections, sometimes at pressures as low as 7,000 kgm. The high temperature has a perceptible weakening effect on the tubing, since the same type of connection had been previously used to 12,000 kgm. in the work on mercury at 20°. Various other types of connection were tried with this first form of apparatus, but none with permanent success. Finally, after six explosions, the attempt to use this form of apparatus was entirely given up, since for one thing, the labor of drilling each new piece of tubing with a hole 1/16 of an inch in diameter and 16 inches long is considerable. However, the data obtained at the lower pressures with this apparatus are perfectly reliable, and form an important part of the data of this paper.

To prevent rupture of the connections, a piece of apparatus much like that finally used was constructed, but which had no connections, everything being made out of one piece of steel. This necessitated drilling a hole 1/8 of an inch in diameter through a piece of steel 30 inches long and 5 inches in diameter, turning the steel to 1½ inches over the middle third, and to the dimensions given above for the cylinders at the two ends,

hardening in oil, seasoning by subjecting to 17,000 kgm. at 200°, and finally machining to the final size after the preliminary stretching. Some measurements had already been made with this apparatus when a flaw developed in the steel which made the whole apparatus valueless. The flaw developed rapidly into a crack through which the kerosene could be forced in a stream.

The risk of flaws in the steel, as exemplified by this accident, is one which is apparently unavoidable in work at very high pressures. Several pieces of Krupp's best chrome nickel steel have previously developed flaws under high pressure, but it was a great surprise to find a flaw in this apparently perfectly homogeneous product of the electric furnace. That the flaw was very small is shown by the fact that the steel had withstood the first application of 17,000 kgm. at 200°.

Rather than run the risk and lose the time of making another piece of apparatus, an attempt was then made to design a form of connection which should not have the weakness of the other, and the attempt was entirely successful. The packing is a thin ring of lead confined between two Bessemer rings. The lead gives the initial tightness, and at the high pressures the soft Bessemer rings become sufficiently deformed to give tightness. The connection has not leaked or broken once in several months of use.

Besides the two forms of apparatus described above for high pressure a third form was used to find points at approximately atmospheric pressure. The necessity of this was not contemplated in the original plan of the work, but an examination of the existing data showed rather large discrepancies in the values for the change of volume (ΔV) on melting at atmospheric pressure, so that a redetermination of these data became necessary. The chief possibility of error in previous work, apart from impurity, seems to have been the formation of unfilled cracks, and uncompensated capillary effects. To avoid this, these determinations were made at a slight pressure, about 60 kgm., and then extrapolation made from 60 to 1 kgm. The change of ΔV with pressure is so small that this can be done without danger. The readings with this apparatus may also be used to give by extrapolation an approximate value of the freezing temperature at atmospheric pressure, but the extrapolation is sometimes uncertain, and the freezing point determined in this way is not so good as that directly measured. However, the freezing point so found may be of some value, and it is given in those cases where it was not determined by direct measurement.

The apparatus for the low pressure measurements is in essentials the same as that used for high pressures. First there is a cylinder of known

cross section in which there is a moving piston. This piston was actuated by a screw instead of by a hydraulic press, and the connection between the screw and the piston was a positive one, so that the piston could be either advanced or withdrawn. The position of the piston was measured as usual with a micrometer. To avoid error from the distortion of the piston or the wearing away of the packing, the piston was made hollow, and a rod was led through the piston and through the packing to the washer retaining the packing at the inner end. The position of the free end of this rod evidently gives directly the position of the upper surface of the liquid in the cylinder. This cylinder connects with a pressure gauge (a Geneva Bourdon gauge was accurate enough) and a second cylinder, containing the substance to be investigated, which was placed in a thermostat. The procedure in making measurements was to vary the temperature at constant pressure, instead of to vary the pressure at constant temperature as in the high pressure measurements. The data give the means of plotting volume against temperature, from which the discontinuity of volume at the freezing temperature may be found graphically. Because of the low pressures used with this apparatus, it was possible to enclose the liquid under investigation in a glass bulb with a mercury seal, instead of a steel bulb, as was necessary at the higher pressures. In this way somewhat greater purity was ensured. The use of the glass also allowed examining the liquid after the experiment, to be sure that none of the transmitting fluid had found its way to it. In no case had this happened. To further ensure purity, no glass bulb was used more than once. The bulbs were filled by boiling the liquid into them under reduced pressure, in the same way as for the steel bulbs. The liquid transmitting pressure in this low pressure experiment was a mixture of water and glycerine, instead of kerosene, which was used at the high pressures. Corrections for the thermal expansion of the glycerine and water on passing from one clyinder to the other were determined and applied in the same way as for the kerosene at high pressures.

Procedure.—This was in most respects like that used either in the work on ice[18] or on twelve liquids[17]. A brief summary will suffice. The purified liquid was boiled into the bulb under reduced pressure to exclude all air, and its quantity determined by weighing. The apparatus was then assembled, the upper thermostat adjusted to 35°, the zero of the manganin coil determined, initial pressure of 1,000–2,000 kgm. applied through the by-pass, the by-pass shut off by pushing in the piston, and then the lower thermostat adjusted to the desired temperature. Pressure was now increased beyond the freezing point sufficiently far to ensure complete freezing, and then the pressure decreased, and readings made

of the position of the piston for about 700 kgm. on each side of the melting point. Ordinarily four points were found above the melting point and three below it, with two determinations of the equilibrium pressure, one from above and one from below, with the liquid about two thirds melted. The results were plotted on a large scale, and the change of volume calculated from the discontinuity at the melting point. The temperature was then changed and the next point found in a similar manner. Ordinarily the points were obtained with increasing pressure and temperature. During one experiment on a single substance the apparatus was left with the pressure continuously at least as high as the initial value. This might be for three or four days. The procedure in finding the point at approximately atmospheric pressure has been indicated, the temperature being varied a few degrees at a time at constant pressure, instead of the pressure being varied at constant temperature.

Corrections.—Several corrections were to be applied, but these have been so carefully described in previous papers that a mere enumeration will suffice; a correction for slight variations in temperature of the manganin coil (in the final form of apparatus there was no such correction), a correction for the distortion by pressure of the cylinder containing the moving piston, a correction for the thermal expansion of the transmitting fluid on passing from one cylinder to the other,* a correction necessary only with the first form of apparatus for slight variations of temperature of the cylinder containing the manganin coil, and finally corrections not peculiar to this particular work, such as corrections for the lack of uniformity of the bridge wire, or corrections for the thermometers, which were mercury thermometers, calibrated at the Reichsanstalt or at the Bureau des Poids et Mesures.

Accuracy.—The accuracy of the melting curves, *i. e.*, the curves showing the relation between melting temperature and pressure, was limited only by the accuracy with which pressure could be determined with the manganin coil. This was as good as .1 per cent. at the higher pressures. The coil was calibrated several times during the course of the experiment by determining with it the freezing pressure of mercury at 0°, the coil being at 35°. There was no change in the coil of so much as 0.1 per cent. during the experiment. The freezing pressure of mercury at 0° was taken as 7,640 kgm., and the relation between pressure and change of resistance was assumed to be linear. (For further particulars on this matter see Proc. Amer. Acad., vol. 47, No. 11, Dec., 1911.)

The accuracy of the values for ΔV is not so high as that for the equi-

* This is the most important correction, and may be as high as 6 per cent.; it was entirely overlooked by Tammann.

librium pressures, chiefly because it is seldom possible to entirely eliminate a slight rounding of the corner at the discontinuity of the curve of volume against pressure. This source of error has also been always present in all previous determinations of ΔV at atmospheric pressure. All the indications are that the special form of apparatus used here avoids this effect at atmospheric pressure more successfully than has yet been accomplished. Of course the error varies greatly with the nature of the substance. Several substances were tried and discarded because they could not be obtained sufficiently pure. Some of the substances show no perceptible rounding of the corners. The order of accuracy can be judged for each separate liquid from an examination of the curves in detail.

The general accuracy of the results is further vouched for by the fact that we have here three independent pieces of data, obtained with different pieces of apparatus at different times; the first with the original high pressure apparatus up to 7,000–10,000 kgm., the second at nearly atmospheric pressure with the low pressure apparatus, and the third with the final high pressure apparatus up to 12,000–13,000 kgm. The inconsistency between the three sets of data is not greater than the discrepancies between readings with the same apparatus.

In addition to the directly measured quantities p, t and ΔV, there are tabulated the latent heat of the change of state and the difference of internal energy between solid and liquid. The latent heat, ΔH, was computed from Clapeyron's equation,

$$\Delta H = \frac{\tau \Delta V}{\frac{d\tau}{dp}}.$$

The computation involves, therefore, the slope of the melting curve. Now the slope of an experimental curve is known with somewhat less accuracy than the points of the curve themselves. To avoid as much as possible error in finding the derivative, two independent methods were used; first the derivative was obtained directly graphically from a large scale drawing, and secondly the melting curve was approximated to by two straight lines, the difference curve drawn, the slope of the difference curve found graphically, and combined with the slope of the straight lines to give the slope of the original melting curve. The two methods agreed very well, usually better than 0.5 per cent., so that we may feel confident that there is no large error in computing the derivatives from the actual melting curves. But aside from the error usually met in finding a derivative, there is here a special source of error operative only at

the low pressures. The curvature of the melting curve decreases rapidly as pressure increases, so that to find the initial curvature as accurately as the curvature at high pressures, a large number of observations would be necessary at the lowest pressures. But the form of apparatus used made it impossible to obtain points at much less than 1,200 kgm. This was due to the sticking of the piston and has been alluded to elsewhere. To avoid it, especially constructed apparatus would be necessary. As a result, the slope at atmospheric pressure of all the curves, and hence the latent heat, is much more in doubt than at any higher pressure. The agreement between the latent heat at atmospheric pressure, computed in this way, and that found by other experimenters by direct experiment, is not very good. In those cases in which reliable direct measurements of the latent heat exist, they have been accepted, and the most probable value of the initial slope computed backward from the accepted value of the latent heat. But unfortunately, the latent heat has been directly measured for only a few of the substances used here. For the other substances it must be borne in mind that the initial latent heat listed here may be subject to correction. The numerical details are given under the separate substances.

The change of internal energy differs from the latent heat only by the external work ($p\Delta V$) during change of state. This involves only quantities directly measured, so the errors in the change of energy are the same as those in the latent heat. In particular, the latent heat and the change of energy are practically the same at atmospheric pressure.

In order to avoid the troublesome work of changing units, and to permit the direct substitution of the values given here in Clapeyron's equation, the latent heat and the change of internal energy are given here in mechanical units, kgm. m. per gm. instead of the familiar gm. cal. per gm. To change kgm. m. to gm. cal. multiply by 2.3442.

Materials.—It is of the utmost importance that the materials be as pure as possible; erroneous results by other experimenters have been obtained because of this, as for example when Tammann announced two solid modifications of carbon dioxide, but later found the effect was due to impurity. The materials to be used were selected by running through a catalogue of chemicals and choosing those which were not prohibitively expensive, which it was known could be obtained fairly pure, which had freezing points within the desired range, and for which only one solid modification was known. These were then subjected to further purification, either by fractional distillation or by crystallization from the melt, or in those cases that were practicable, by both methods. The details of the purification by distillation do not require comment. The purification

by crystallization was performed with more care than is perhaps usual. The substance to be purified was placed in the melted condition in a closed glass vessel, within a larger glass vessel, which dipped into a bath kept at constant temperature by a thermostat. The thermostat was then adjusted to a temperature a few tenths of a degree, or perhaps as much as 1.5° (depending on the purity of the substance) below the freezing point of the pure substance. After temperature equilibrium had been attained and the substance was in a slightly subcooled condition, it was inoculated with a minute crystal, and crystallization allowed to take place. Transfer of heat from the bath to the substance took place across an air space, and was therefore slow. Crystallization might continue in some cases for a couple of days. The remaining liquid was then drained off by inverting the glass vessel. The draining occupied several hours. During the draining the temperature of the thermostat was raised a few tenths of a degree in order to melt off more perfectly any layer of impurity clinging to the crystals. The advantages of the method are the very slow crystallization, and the fact that one can be perfectly sure that there is not enough impurity present to depress the freezing point as much as the depression artificially maintained by the thermostat.

No special analysis is necessary to show the amount of purity finally attained, because the conditions of the experiment themselves impose one of the sharpest tests that could be applied. If the substance is perfectly pure it will all freeze sharply at one temperature, but if it is impure, the impurity will remain in the liquid as crystallization progresses, becoming more and more concentrated, so that the freezing temperature will drop as freezing proceeds. Or if the freezing takes place at constant temperature, as here, the freezing pressure will increase as the liquid approaches complete solidification. This will be shown by a rounding of the upper corner (where melting begins) of the curve of volume against pressure. It has been already stated that in only a few cases was it possible to entirely get rid of the rounding, but it was never allowed to become large enough to raise doubt; if it did the liquid was discarded, or further purified. It was very seldom that the rounding was perceptible more than 200 kgm. beyond the freezing point, and the curve from which extrapolation was made was usually run 700 kgm. beyond the point.

One other effect of impurity is to greatly slow the reaction, so that it may be necessary to wait hours for equilibrium. The reason for this is evident. As the liquid crystallizes the pure substance separates, leaving an excess of impurity in the neighborhood of the freshly formed crystal. Further freezing cannot now continue until the excess of impurity has

been removed by diffusion into other parts of the liquid. But at high pressures the diffusion takes place very slowly because of the greatly increased viscosity. One striking example of this was found while working on monochloracetic acid. After setting up the apparatus the acid was found to become gradually impure by attacking the steel envelope. Three points at high pressure were determined. The progressive gain of impurity was shown not only by the much greater rounding of the corners at the last reading (which was at lower pressure than the first two), but by the exasperating slowness of the reaction. The impurity of this one substance finally became so great that it was not worth while to attempt any more readings.

The slowness of the reaction furnishes, therefore, a further rough test of the purity of the substance. Thus Tammann mentions that he was troubled by the slowness of freezing of a number of his substances, while no such trouble was found here. The presumption is that Tammann's materials were impure. An example is the case of sodium. Tammann found a very slow reaction, while in the present work the reaction ran as rapidly and as cleanly as one would expect from a metal, as rapidly as for mercury, for example.

In some cases actual experiment showed that the commercial materials were pure enough. Examples are phosphorus and sodium. The details of the purification are to be found under the data for the separate liquids.

Unsuccessful attempts were made to purify acetophenone and para-xylol. Two crystallizations of acetophenone did not raise the freezing point more than 0.5°, from 19.1° to 19.6°, although the pure substance melts at 20.5°. Two distillations of para-xylol failed to give a liquid that approximated to a constant boiling point. An attempt was also made to purify acetone. This was Kahlbaum's best, "from bisulfite," and would have been judged to be perfectly pure from the constancy of the boiling point, but the freezing under about 10,000 kgm. was spaced over a wide pressure interval. Monochloracetic acid was also tried and discarded because it collected impurities from the pressure apparatus, not because it could not be sufficiently purified initially.

Depression of Freezing Point under Pressure.—One question of interest in this connection is as to the variation of the depression of the freezing point by impurity with pressure. It admits of simple thermodynamic treatment as follows.

We shall find it easy to deduce this relation by considering first the equilibrium between pure liquid and pure solid, both being at the same temperature, but the hydrostatic pressure on one being different from that on the other. Let us suppose that the liquid (1) and the solid (2) are in

equilibrium under normal conditions at p and t. The temperature of both phases is now raised by Δt, and the pressure on the liquid kept at its original value. We require to find the increment of pressure (Δp) on the solid, so that the liquid at p and $t + \Delta t$ may be in equilibrium with the solid at $p + \Delta p$ and $t + \Delta t$. The relation may be found by an obvious thermodynamic cycle to be

$$\frac{\Delta t}{\Delta p} = \frac{-v_2 t}{\Delta H},$$

where ΔH is the latent heat of transformation. Δt and Δp are, therefore, of opposite sign.

We now apply this formula to determine the depression of the freezing point. Given pure (1) and (2) in equilibrium at p and t, and impure (1) in equilibrium with pure (2) at p and $t - \Delta t$. We require to find Δt. The direct contact between pure (2) and impure (1) may be separated by an intermediate step. Impure (1) at p and $t - \Delta t$ shall be in equilibrium with pure (1) at $p - \Delta p$ and $t - \Delta t$, and the pure (1) at $p - \Delta p$ and $t - \Delta t$ shall be in equilibrium with pure (2) at p and $t - \Delta t$. Under these conditions we shall evidently also have impure (1) at p and $t - \Delta t$ in equilibrium with pure (2) at p and $t - \Delta t$. The decrement of pressure is evidently the osmotic pressure of the dissolved impurity. Now the formula deduced above gives a relation between Δt_1 and Δp (see Fig. 1). We have, therefore, the two equations

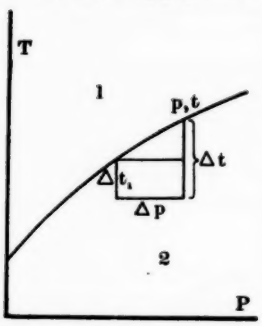


Fig. 1.

Diagram for the depression of the freezing point by impurities.

$$\frac{\Delta t_1}{\Delta p} = \frac{v_2 t}{\Delta H},$$

and

$$\Delta t_1 = \Delta t - \Delta p \frac{d\tau}{dp}.$$

Whence

$$\frac{\Delta t}{\Delta p} = \frac{v_2 t}{\Delta H} + \frac{d\tau}{dp} = \frac{v_1 t}{\Delta H},$$

and finally,

$$\Delta t = \frac{v_1 t}{\Delta H} \Delta p.$$

This gives the depression of the freezing point in terms of the osmotic pressure of the dissolved impurity. Now Δp does not change much with

increasing pressure, since for impurities of slight concentration it is equal to the pressure that would be exerted by the impurity in the form of a gas occupying the same volume. ΔH changes only slightly on the melting curve, as will be shown later. v_1 decreases and t increases as pressure increases; the two partly neutralize each other. We need expect, therefore, that the depression of the freezing point due to a given quantity of dissolved impurity will not change markedly on the freezing curve, what change there is probably being in the direction of an increase.

(*To be continued in following number, p. 153.*)

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE SEVENTIETH MEETING.

A JOINT meeting of the Physical Society with Section B of the American Association for the Advancement of Science was held in the physics lecture room of the Georgia School of Technology, Atlanta, Ga., December 29, 1913, to January 3, 1914. The presiding officers were Past-President E. L. Nichols (in the absence of President B. O. Peirce, of the Physical Society) and Vice-President A. D. Cole, of Section B.

The annual business meeting of the Physical Society was held Thursday forenoon, January 1, 1914. Messrs. A. Zeleny and N. E. Gilbert acted as tellers and reported the result of the mail ballot for officers for 1914.

No nominee for president having a majority of all votes cast, the Society chose Ernest Merritt president by ballot.

As Mr. Merritt had been elected Vice-President by the mail ballot, a new ballot resulted in the choice of K. E. Guthe as Vice-President.

The following officers were declared elected by the mail ballot:

Secretary: A. D. Cole.

Treasurer: J. S. Ames.

Members of the Council: D. C. Miller and G. K. Burgess.

Managing Editor: Frederick Bedell.

Members of Editorial Board: A. G. Webster, C. E. Mendenhall, H. A. Bumstead.

The secretary presented the reports of the treasurer and of the managing editor of the PHYSICAL REVIEW. These reports will be printed and mailed to all members.

It was announced that the Council had voted to continue the existing arrangement with the publishers of Science Abstracts for the year 1914.

The session of Tuesday afternoon, December 30, was in charge of Section B, and was devoted to papers of general interest as follows:

Address of the Retiring Vice-President of Section B, "The Methods of Physical Science; to what do they Apply?" A. G. WEBSTER. (Read by A. D. Cole.)

The Factors of Climatic Control. W. J. HUMPHREYS.

Isostasy and the Size and Shape of the Earth. WM. BOWIE.

On Thursday forenoon there was a joint session with Sections B and C, with this program:

Geochemical Research. JOHN JOHNSON.

The Ternary System; Lime—Alumina—Silica. G. A. RANKIN.

Seismology. OTTO KLOTZ (Dominion Observatory, Ottawa, Canada).

The Present Status of the Magnetic Survey of the Earth. L. A. BAUER (presented by W. J. Humphreys).

At the other three sessions of the meeting the following papers were presented:

The Illumination-Current Relationships in Potassium Photo-electric Cells. HERBERT E. IVES.

Range of Alpha-Particles in Air at Different Temperatures. ALOIS F. KOVARIK.

Counting the Transmitted and Reflected Beta-Particles. ALOIS F. KOVARIK and L. W. MCKEEHAN.

An Absolute Method of Determining the Ballistic Constant of a Moving-coil Galvanometer. PAUL E. KLOPSTEG (presented by Anthony Zeleny).

Contributions to the Thermodynamics of Saturated Vapors. J. E. SIEBEL.

Experimental Tests on an Artificial Cable at 700 Cycles. H. G. HEIL.

The Energy Absorption of Condensers for High-frequency Oscillations excited by the Lepel Arc. A. D. COLE.

Binaural Beats and the Character of the Sound-conducting Paths between the Ears. G. W. STEWART.

The Mobility of Ions at Different Temperatures and Constant Gas Density. H. A. ERIKSON.

Thermo-electromotive Force produced when the Two Metals forming a Junction are not at the Same Temperature. S. L. BROWN.

Why some Winters are Warm and others Cold in the Eastern United States. W. J. HUMPHREYS.

Physical Characteristics of the Vowels. DAYTON C. MILLER.

Absorption of Beta-Rays by Gases. ALOIS F. KOVARIK.

Calculation of the Size of Wire for a Damping Rectangle to Produce Critical Damping in a Moving-coil Galvanometer. PAUL E. KLOPSTEG (presented by Anthony Zeleny).

A New Fuorescence Spectrum of Uranyl Chloride. EDWARD L. NICHOLS and ERNEST MERRITT.

Preliminary Note on Fluorescence Spectra of Aqueous Solutions of Uranyl Salts at Low Temperatures. EDWARD L. NICHOLS and ERNEST MERRITT.

A System of Color Standards for the Practical Measurement of Color. H. E. WETHERILL. (By title.)

On the Thermions Produced by Platinum. CHARLES SHEARD. (By title.)

Discharge Potentials across Very Short Distances. EDNA CARTER.

Adjournment Thursday noon, January 1, 1914.

A. D. COLE,
Secretary.

ON THE THERMIONS PRODUCED BY PLATINUM.[1]

BY CHARLES SHEARD.

THE results presented here are in continuation of the work reported in the PHYSICAL REVIEW for October, 1913.

1. The positive thermionic currents obtained on the *initial* heating of the wire over the range of temperature from 530–850° C. followed the Richardson law $i = AT^{\frac{1}{2}}e^{-b/T}$.

2. Upon heating the wire under positive potential until the " steady-valued " or " slow decay " current condition obtained and upon using the current values thus found in the Richardson formula, two distinct linear relations held between $\log i - \frac{1}{2}\log T$ when plotted against $1/T$, (where i = thermionic current and T = absolute temperature). The ratio of the tangents of the angles which these lines make with the temperature axis was found equal to about 0.6. The first range of values covered temperatures from about 600 to 725° C.; the second from 725 to 850° C.

3. With continued heating under positive potential it was found that the slope of the line at high temperatures gradually changed and assumed a position nearly parallel with that of the temperature-current relations obtained at the lower temperature range. This is interpreted to mean that there are two sources capable of producing ionization and is in agreement with data obtained by Richardson indicating a value of e/m = 32–36 for the initial period of heating and giving, under further treatment, a value of e/m = 25.

4. With further heating under potential a condition was reached in the lower temperature range in which the ionization currents were smaller at higher temperatures than those obtained at the preceding lower temperatures.

5. The effect of moisture upon the positive thermionic currents has been carefully investigated. At a definite temperature the positive decay with time curve was obtained; when the steady-valued current period was reached the wire was dipped in distilled water. This process was repeated seriatim some half dozen times. In each instance a very considerable increase in ionization currents was produced, the effect being the greatest in the case of the initial addition of water. This increased ionization fell away very quickly with time. Upon testing the curves thus obtained by plotting the logarithm of the difference between the actual current and the steady leak versus the time, two straight lines were obtained in each case, the slope of the line obtained from the readings during the first few minutes being greater than that of the second line representing the decay with time from the fifth minute on. In all cases the lines intersect at the time point 2.5–3.5 minutes. These and similar results, it is believed, are sufficient to show the effect of the presence of traces of *water vapor* on the initial positive ionization. It will be shown that the results of Richardson[2] as to the so-called activity induced by air and the activity

[1] Abstract of a paper presented at the Atlanta meeting of the American Physical Society, January 1, 1914.

[2] Phil. Mag., Vol. VI., 1903.

induced by hot wires at higher pressures as well as the recent work of Klemenciewicz[1] on the restoration of thermionic emission when metals are heated in various gases, can be wholly explained as due to the presence of water vapor.

6. Following the experiments with water vapor, the wire was removed and washed in nitric acid. When again tested at the same temperature as that used in the water experiments it was found that the initial current-time curve was almost identically duplicated. This and other facts point to the conclusion that the dissociation of water vapor until temperature and potential produces positive H ions and that the oxygen in turn forms oxides removable in hot nitric acid. Heating the wire without the application of potential does not give the effects referred to above.

7. With continued usage, however, the ability of the wire to produce increased ionization when cleaned in acid fell off markedly, indicating that there are present in the wire one or more substances which give thermions not due to chemical action.

8. The effect of heating the wire in hydrogen and carbon dioxid was investigated when the wire was in a condition of producing extremely small thermionic currents. Increased currents were obtained after ten minutes' heating in hydrogen which fell off to values of the order of the currents obtained before such treatment in the course of two or three minutes. The same effects in general were obtained in carbon dioxide. These effects do not point to the conclusion of Horton and others that heating in hydrogen, etc., causes a subsequent emission of the absorbed gases as ions. Rather is it to be believed that small traces of water vapor or hydrogen (due to its reducing action on the surface of the wire or to its recombination with oxygen producing water at the surface of the wire) constitute the cause of this increase.

9. The wire when initially tested, and for some time after, showed an increased positive emission after the wire had been heated for a few minutes under negative potential and at such temperatures as to cause a negative ionization current. In time, however, the wire reached a condition in which such a treatment produced no effect on the subsequent positive currents. These effects may be due to—(1) previous removal of material in the wire capable of producing ions or (2) to the inability of the surface of the wire after oxidation to further combine with oxygen, hence permitting no permanent dissociation of water vapor.

10. The wire was finally gotten into a condition such that with increase of temperature by stages of 20° from 550–900° C. the ionization currents rose to a maximum at a certain temperature within the range 600–675° C. and then fell off with increase of temperature until the higher temperature range of 825–900° C. was reached. In this latter region the current values rose with increase of temperature, but the current value at 900° C. was in most cases several times less than at 600–650° C. This maximum at lower temperatures did not, under many repetitions, appear at the same temperature but did occur within the 600–650° range. A time effect was looked for and it was found that this

[1] Ann. der Phys., 1911.

maximum was reached in 7–10 minutes of heating without any apparent connection with increase of temperature. The paper, when published, will present and discuss three possible explanations.

11. There are, then, apparently two general sources of thermions: (1) external, not permanent but very effective in the initial stages, and (2) internal, permanent. The first source is probably chiefly water vapor, the second consists of impurities present in the form of salts.

OHIO STATE UNIVERSITY,
December 27, 1913.

THE CHARACTER OF INTERAURAL SOUND CONDUCTION INDICATED BY BINAURAL BEATS.[1]

BY G. W. STEWART.

SOUND conduction of the bones of the head is well known. Experiments in sound localization with two tones of the same frequency but of different phase, presented one to each ear, have shown the importance of interaural sound conduction. Rostosky assumes a conduction with a lag due to longer path; Wilson and Myers assume in addition a change of phase of 180°. These theories do not account for the maxima of apparent intensity found when two tones differing slightly in frequency are presented one to each ear. The maxima as observed first by Rostosky and later independently by the writer occur as follows:

1. With rapid cycles of recurring equal phase, the cycles being less than one or two seconds, a maximum of apparent intensity occurs at zero phase difference, as has long been known, but with the cycle of greater length additional maxima appear at phase differences $180° - \delta$ and $180° + \delta$, the former occurring apparently in the ear having the tone of greater frequency.

2. With cycles greater than one second in length, the additional maxima increase in intensity with increasing cycle length until they appear of greater intensity than the original maximum.

The additional facts found by the writer are:

3. The quality of the tone at zero phase maximum is the same as that of the exciting tones, but the quality of the tone at the additional maxima is noticeably different, being less pure.

4. The value of δ is independent of the duration of one cycle, depending only on the frequency of the tones.

5. The values of δ with varying frequency as determined by Dr. Stiles and the writer are: with 256 d.v., 64.8°; 128 d.v., 54°, and 64 d.v., 32.4°.

6. Theoretical considerations assuming simple sound conduction and using the sum, the ratio, and the differences of intensities at the ears, and also the individual intensities, do not produce results consistent with the experimental facts.

[1] Abstract of a paper presented before the American Physical Society at Atlanta, December 31, 1913.

From a detailed consideration not outlined here, there appear the following conclusions:

1. That the causes producing the zero maximum are not those which produce the additional maxima.

2. That conduction from one ear to the other produces a resulting variation of intensity in each ear, and that the maximum and minimum occurring with rapid cycles can be accounted for if the sum of the two ear intensities be regarded as the determining factor. (The importance of this factor has already been pointed out by the writer.)

3. That the experimental values of δ given agree with the theory that the additional maxima are caused by forced vibrations, for tan δ is proportional to the frequency within experimental error. This agreement is striking and demands further investigation.

PHYSICAL LABORATORY,
STATE UNIVERSITY OF IOWA.

AN ABSOLUTE METHOD FOR DETERMINING THE BALLISTIC CONSTANT OF A MOVING-COIL GALVANOMETER.[1]

BY PAUL E. KLOPSTEG.

FROM the equation for damped periodic motion of a galvanometer coil, expressing the condition for the discharge of a quantity Q of electricity through the coil at rest, the value of the first maximum displacement is found by the usual method of differentiation. This value represents the ballistic throw of the slightly damped galvanometer. From the expression so found the equation for the ballistic constant is obtained. In the transformation a substitution is made which is based upon the equation for the damped coil method of measuring magnetic fields. The resulting expression is

$$K_1 = \pi \sqrt{\frac{I_0 \epsilon^{\lambda}}{10^7 R T_0 (\Lambda - \lambda)}},$$

this value of K_1 being equal to the number of coulombs per radian. I_0 is the moment of inertia of the coil, T_0 its period and λ its logarithmic decrement on open circuit, and Λ its logarithmic decrement with R ohms in the galvanometer circuit.

When the value of λ is about 2.5 per cent. of π, the value of K_1 is too large by 0.1 per cent., the difference increasing as λ grows larger. The following more exact formula may then be used:

$$K_2 = \epsilon^{\frac{\lambda}{\pi} \tan^{-1} \frac{\pi}{\lambda}} \sqrt{\frac{I_0}{10^7 R T_0} \frac{\pi^2 - \lambda^2}{\Lambda - \lambda}}.$$

An explanation is offered for the frequently observed difference between the

[1] Abstract of a paper presented before the American Physical Society at Atlanta, December 31, 1913.

values of the ballistic constant in a given instrument with a strip or ribbon upper suspension, on the two sides, A and B, of the scale. This difference is due principally to a certain amount of torsion in the lower suspension which necessitates a corresponding amount of "counter torsion" in the upper suspension in order to keep the coil in the position of the null reading. The effect of torsion in a strip suspension is to shorten it, the case resembling that of a bifilar suspension for angles less than 180°. For a throw in one direction, say A, the coil must be raised; in the opposite direction the turning moment of the force of gravity acts in the same direction as the electromagnetic torque. Consequently with a given quantity of electricity the throw in the direction B is greater than in the direction A.

The same "bifilar effect" introduces an error into the determination of I_0 of a coil by the comparison of vibrations method when a strip is used as the suspension fiber, unless the masses of the coil and of the comparison disk, as well as their amplitudes, are the same. The error due to this effect becomes negligible if a wire of circular cross-section is used as the suspension fiber.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA.

RANGE OF α-PARTICLES IN AIR AT DIFFERENT TEMPERATURES.[1]

BY ALOIS F. KOVARIK.

THE range of α-particles in any substance depends on the nature and the number of atoms in the path. And we find, therefore, that the range varies inversely with the pressure of a gas; similarly, we should expect that the range varies inversely with absolute temperature. This has been tacitly assumed to be true. In some experiments on the ionization by the α-particles I have found it convenient to test this experimentally between 90° and 362° absolute. The apparatus and method were after Geiger and Nuttall. Bulbs used as ionization vessels were of two sizes, 5 cm. and 9 cm. radius, respectively. The bulbs were metallic. The temperature was obtained by means of a thermocouple placed near the center of the bulb. The α-ray substance used was a polonium plate of about 4 mm. diameter. The lowest temperature was obtained by immersing the bulb in liquid air and the highest temperature by immersing the bulb in boiling water. Intermediate temperatures were at room temperature and the temperature obtained when the apparatus was packed in ice. The pressure-ionization curves gave sharp breaks for the ordinary temperatures, but at the low temperature the change was not as abrupt, a rounded bend being obtained. This was no doubt due to some convection currents (which must have existed as the neck of the bulb protruded from the liquid air). However, the pressure at which the α-particle just reached the walls of the bulb could be fairly accurately determined from the

[1] Abstract of a paper presented at the Atlanta meeting of the American Physical Society, December 30, 1913.

straight lines below and above this pressure. The following table shows the experiments tried and the results obtained:

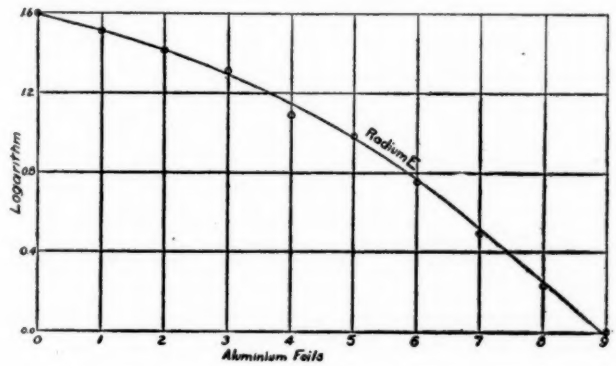
Temp. Absolute.	Size of Ionization Vessel.	Range Abs. Temp.
90.0	5 cm.	0.0125
273.7	5 cm.	.0130
297.3	5 cm.	.0130
298.0	5 cm.	.0129
298.0	9 cm.	.0129
300.0	9 cm.	.0129
362.0	9 cm.	.0131

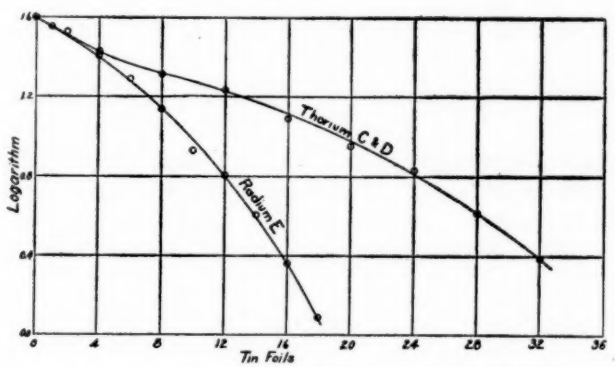
PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA.

COUNTING THE TRANSMITTED AND REFLECTED β-PARTICLES.[1]

BY ALOIS F. KOVARIK AND LOUIS W. MCKEEHAN.

RECENTLY Dr. H. Geiger announced a simple method for counting α- and β-particles.[2] This method depends on the point discharge set up when a few ions are produced near a point at a potential close to that required for a continuous discharge.





[1] Abstract of a paper presented before the American Physical Society at Atlanta, December 31, 1913.

[2] Verh. d. Deut. Phys. Ges., XV., p. 534, 1913.

Measurements, by this method, on the number of β-particles transmitted and reflected by thin foils of aluminum and of tin were made, using for the source radium E and thorium active deposit. The results show that the number of β-particles transmitted decreases more rapidly than if the exponential law held as it does hold in measurements of absorption by the ionization method. In the reflection experiments, the ratio of the number of reflected β-particles to the number incident was found smaller than the ratio of the ionization of the reflected rays to the ionization of the incident rays, as found by Schmidt and one of us.[1] In both classes of experiments, the absorbing or reflecting material was close to the source of rays and at some distance from the counting chamber.

The figure shows that the logarithmic curves deviate from the straight lines to be expected from the exponential law. The increase of ionizing power with the decrease of velocity of the β-particles, due to passage through matter, doubtless explains the effects observed.

The comparatively small number of β-particles counted in these experiments (60,000) makes it undesirable at present to state the results quantitatively.

Discharges from the point due to γ-radiation were small in number under the conditions of the experiments, but were always measured and corrected for.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA.

ABSORPTION OF β-PARTICLES BY GASES.[2]

BY ALOIS F. KOVARIK.

THE preliminary work on the absorption of β-particles, namely from radium D and radium E, was reported at a previous meeting of this society. The principle of the method used in the investigation is to allow the particles to pass through a definite distance in the gas before entering a shallow ionization chamber (2 or 3 mm. deep). By increasing the pressure of the gas, the absorption becomes greater, but the ionization in the ionization chamber also becomes greater. If the pressure is within twenty atmospheres the ionization is proportional to the pressure. All measurements were made within this pressure. Consequently, the ionization reading is reduced to what it would be at one atmosphere. The mean path of the β-particles is found graphically. By changing the pressure the absorption curve is obtained. The values obtained for the coefficient of absorption for different distances of the active material from the ionization chamber were concordant when the metallic pressure apparatus was lined with thick paper, thus minimizing the reflected radiation effect. This also shows that the graphical method of finding the mean path of the β-particles is feasible. The measuring instrument was C. T.

[1] Schmidt, Ann. d. Phys., XXIII., 671, 1907; Kovarik, Phil. Mag., XX., 849, 1910.

[2] Abstract of a paper presented before the American Physical Society at Atlanta, December 31, 1913.

R. Wilson's inclined electroscope in some experiments, ordinary Dolezalek electrometer and Erikson's modification of Dolezalek's electrometer. The rate method and Townsend's null method were both used in taking readings, the null method being found the more satisfactory.

The radiations examined are those from radium D, radium E, uranium X, actinium active deposit, thorium active deposit. The soft radiation was studied by obtaining the differential curve and it was found rather difficult to obtain accurate results.

The results are given in the table below for the two gases used, air and carbon dioxide.

Substance.	Coefficient of Absorption in— Air.	Carbon Dioxide.
Radium E	0.0151 cm.	0.0298 cm.
Radium D (hard)	0.086	0.157
Radium D (soft)	0.64	1.48
Uranium X (hard)	0.0063	0.0116
Uranium X (soft)	0.12	0.24
Actinium Active Deposit (hard)	0.0091	0.0175
Actinium Active (Deposit (soft)	0.35	
Thorium Active Deposit (hard)	0.00683	0.01293
Thorium Active Deposit (soft)	0.09	0.14

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA.

THE MOBILITY OF IONS AT DIFFERENT TEMPERATURES AND CONSTANT GAS DENSITY.[1]

BY HENRY A. ERIKSON.

THE mobility of ions at different temperatures and at constant pressure was determined by Kovarik and by Phillips. The agreement in their results is quite close. The writer has felt that a determination of the mobility at constant gas density ought, however, to be made as the conditions to which the ions are subject at the lower temperatures at least are not necessarily the same in this case as in the case of constant pressure.

The α rays from polonium were used as the ionizing agent. The ions were drawn towards a wire grating through which some of them passed and became subject to an alternating field. The time required to charge the electrometer to a given potential was measured. The reciprocal of this time, *i. e.*, the current is proportional to the frequency. By using various values for the frequency and plotting, the frequency (n) necessary to give no current is obtained and the mobility calculated from the relation

$$k = \frac{4d^2n}{v},$$

where d is the distance from the grating to the plate connected to the electrometer and v the difference of potential.

[1] Abstract of a paper presented at Atlanta meeting of Physical Society, December, 1914.

The vessel was air tight and was immersed in CO_2 snow and liquid air during the measurement at the two lowest temperatures. The results obtained thus far are as follows in centimeters per gradient of one volt. The density being that of air at 0° C. and 76 cm. pressure.

Temp. °C.	k_+	k_-
20	1.35	1.89
− 64	1.34	1.82
−180	1.20	1.24

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
December 22, 1913.